

# **An Interdisciplinary Study of Environmental Pollution by Lead and Other Metals**

**Progress Report**

**May 1, 1974 to September 30, 1975**

**NSF RANN GRANTS GI-31605 and ERT 74-24276**



University of Illinois at Urbana – Champaign

**INSTITUTE FOR ENVIRONMENTAL STUDIES**

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# **An Interdisciplinary Study of Environmental Pollution by Lead and Other Metals**

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Progress Report PR5

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## I. INTRODUCTION

This progress report for the University of Illinois Metals Task Force covers the period from May 1, 1974 to October 1, 1975. Included are reports from the plant response, urban dust, synthesis and modeling, and analytical laboratory groups. A completion report for the project's ecosystem studies was published in August, 1975.

### HISTORY AND ORGANIZATION

The concept of a wide-scale, interdisciplinary project on environmental contamination by lead originated in 1968 with Professors R. L. Metcalf and Ben B. Ewing. Discussion with interested faculty resulted in the formulation of a proposal for an exploratory and planning grant from the National Science Foundation IRRPOS program. After the exploratory phase from July 1, 1970, to October 31, 1971, three additional grants from the National Science Foundation RANN program have been received for continuation of these studies. Originally conceived as a mixed multidisciplinary-interdisciplinary project, it has gradually developed into a truly interdisciplinary research effort.

The current organization of the project is shown in Figure 1. Professor G. L. Rolfe is the principal investigator and director of the Metals Task Force.

The Research Management Group is composed of the director and assistant director of the Metals Task Force, the director of the Institute for Environmental Studies, and the project group leaders.

### OBJECTIVES

The major objectives of the Metals Task Force have been (1) the development of interdisciplinary research methods on a university campus and (2) an evaluation of the input, distribution, and effects of lead in the environment.

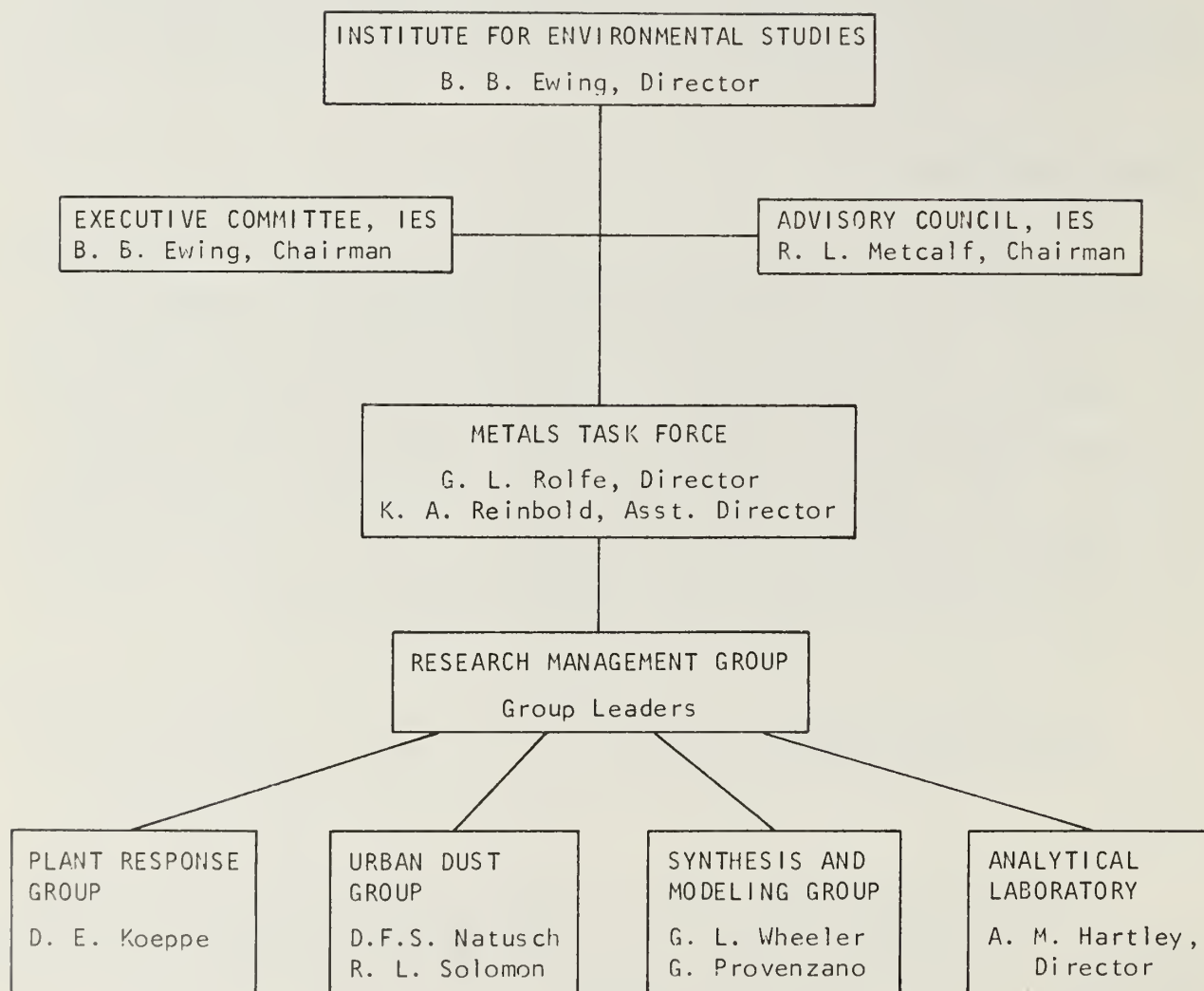


Figure 1. Project organization.

Completed during 1975 were studies of the current distribution of lead in ecosystem components resulting from the use of lead in gasoline as well as a number of studies of the fluxes of lead, the factors controlling those fluxes, and the effects of lead on ecosystem components other than man. The results were presented in the ecosystem group completion report.

During the past year, investigations have focused on two areas: (1) lead effects on terrestrial plant productivity and (2) sources, transport pathways, and forms of lead in the urban environment.



## II. PLANT RESPONSE STUDIES

During the past year, research in the Plant Response Group has progressed in three areas: soils, aerosol deposition and effects, and the effects of environmental factors. Most of the current research is in its second or third year. The microbial-lead interaction studies, however, began within the past year.

### SOILS

#### Environmental Variables which Affect Lead Sorption

##### Lead Sorption to Soils

Determination of lead sorption capacities of selected Illinois soils using titration curves has been completed<sup>1</sup>. The capacity of a soil to sorb or bind  $Pb^{+2}$  may be determined by titrating the soil with a  $PbCl_2$  solution. The addition of lead to the soil slurry results in a shift in pH. The sorption capacity corresponds to the point of maximum curvature in the titration curve. Sorption capacities obtained in this manner are highly correlated with plant uptake of Pb and with sorption capacities obtained from leaching curves and adsorption isotherms. The advantage of the titration technique is that it requires less time and equipment.

A preliminary experiment using roadside soils from southern Illinois has been completed. Based on the results, additional work is being planned for the next funding period. In the preliminary experiment it was found that, because crushed limestone is used as the road base, the areas next to the road which have high lead levels also have high pH values (7.8 to 8.2). A series of soils was collected along a rural highway. Extractable lead, soil cation exchange capacity (CEC), and soil pH were determined. Corn was grown in the soils, and Pb uptake was determined after 42 days' growth in the greenhouse. The results are presented in Table 1.

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<sup>1</sup>References are listed on pages 77-80.

Table 1

Extractable Lead and Lead Uptake by Corn Plants  
from a Series of Roadside Soils

----Roadside Site	Soils----- CEC	pH	Pb Extracted 3N HCl	Pb in Corn Plants ( $\mu\text{g/g}$ )
1M 1A	22.6	7.87	579	2.95
16M 1B	26.6	5.80	71.7	1.77
2A	15.5	5.63	16.3	2.87
East 3A	18.5	7.04	482	3.66
West 3B	23.5	6.05	109	2.42
West 4A	14.5	7.51	89.3	2.10
East 4B	12.7	7.63	170	2.56
1M 5	22.5	7.06	71.3	1.96
1M 6	15.7	8.16	593	3.85
10M 7	17.4	7.93	57.6	3.35
South 8A	21.2	7.75	141	3.28
North 8B	21.6	7.71	521	3.00
10	19.5	7.02	27.8	2.73
11	10.6	6.01	27.7	2.29

A series of lead-treated soils has been anaerobically incubated for periods up to six months. The effects of Eh (Nerst potential) and pH on the release of sorption of lead are being determined but at this time are incomplete.

Relationship of Lead or Cadmium Soil Sorption to Plant Uptake

Corn and Soybeans:

Studies of the effect of soil lead sorption capacity on uptake of lead by corn have shown that the uptake by four-week-old corn shoots grown in lead-amended soils was dependent on the level of lead in the soil relative to the soil's capacity to sorb lead<sup>2</sup>. At any given level of added lead, the uptake

by corn plants was found to decrease with an increase in soil pH, CEC, and available phosphorus. Lead levels in corn were found to be highly correlated with the  $Pb_T/Pb_S$ , where  $Pb_T$  is the total lead in the soil and  $Pb_S$  is the soil lead sorption capacity.

Similar studies were conducted with soybeans<sup>3</sup>. Lead uptake by the above-ground portion of soybean plants was also found to be inversely related to soil CEC and pH, while available soil phosphorus levels did not influence lead uptake. The amount of lead extracted from the soil with the Bray  $P_1$  reagent was highly correlated with lead accumulations in both soybeans and corn. Evidence also indicated that lead accumulation in soybeans is related to the degree to which the total sorptive capacity of the soil for lead is satisfied.

The accumulation of cadmium and its effect on vegetative growth of soybeans in soils with a range of CEC, pH, and available phosphorus were investigated<sup>4</sup>. All three soil variables, as well as  $.01M HCl + .03N NH_4F$  (Bray  $P_1$  reagent) extractable cadmium, were significantly correlated to cadmium accumulation by soybeans. Cadmium uptake decreased as soil pH and CEC increased. Cadmium uptake increased with an increase in available soil phosphorus, a finding which is in marked contrast with the effect of available phosphorus on lead uptake. The growth of soybean shoots was generally depressed when tissue concentrations reached  $3 \mu g Cd/g$  dry weight. Cadmium uptake was not related to soil cadmium levels, but rather to the ratio of added cadmium to the cadmium sorptive capacity of the soil.

Uptake of cadmium by corn was also investigated<sup>5</sup>. Increasing soil CEC and pH resulted in a decrease in cadmium uptake. Available soil phosphorus had little effect on cadmium uptake by corn, although significant interactions between (1) CEC and available phosphorus and (2) pH and available phosphorus were found.

#### Lead and Cadmium in a Model Ecosystem:

The fate of lead and cadmium in a model ecosystem was studied<sup>6</sup>.



Lead and cadmium were added as  $\text{PbCl}_2$ ,  $\text{CdCl}_2$  and in sewage sludge containing these elements. Lead ( $10 \mu\text{g/g}$ ) was added to the solid phase of model ecosystems. The three types of solid phases used were (1) 15 kg silica sand, (2) 1.5 kg Bloomfield soil (sandy loam) with 13.5 kg silica sand and (3) 1.5 kg Drummer soil (silty clay loam) with 13.5 kg silica sand. In all components of the ecosystem (water, alga, daphnia, fish, mosquito larva, snail, sorghum), the greatest amount of lead was taken up in the system using a silica sand solid phase. Less lead was taken up in the system using Bloomfield soil and sand, and the least appeared in the components of the system containing Drummer soil and sand. In separate experiments where sludge was mixed with the solid phase as a source of lead ( $5.5 \mu\text{g/g}$ ) there was less uptake from the Bloomfield and Drummer soils than from the silica sand.

#### Organic Matter Binding of Lead

Before the interactions of lead with soil organic matter could be determined, it was necessary to develop techniques of extraction, fractionation, and purification of humic and fulvic acids, the main organic constituents of soils. In addition, the electrochemical properties of these acids had to be determined.

The classical method for recovering organic matter from soils has been by extraction with a base, usually 0.5 N NaOH. The technique was found to be unsuitable for recovering fulvic acids and an improved extraction procedure was developed using an acetone- $\text{H}_2\text{O}$ -HCl solvent.

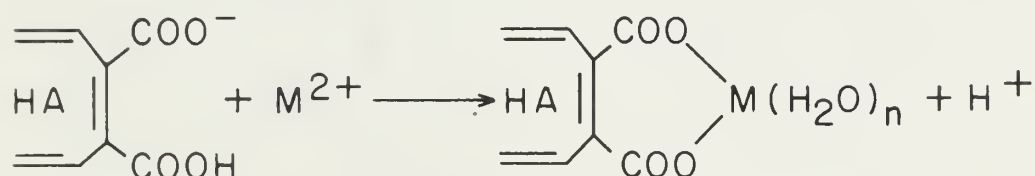
In view of the heterogeneous nature of humic and fulvic acids, not all binding sites can be considered identical. It is likely that multiple sites are involved in complex formation, each having its own characteristic affinity for metal ions. Furthermore, considerable variability in binding strength would be expected for each kind of site because of structural considerations and the proximity of neighboring functional groups. Stability constants calculated from the data were found to increase with decreasing concentrations of the metal ion, thus indicating reduced affinity of humic acids to metal ions as the stronger site became saturated.



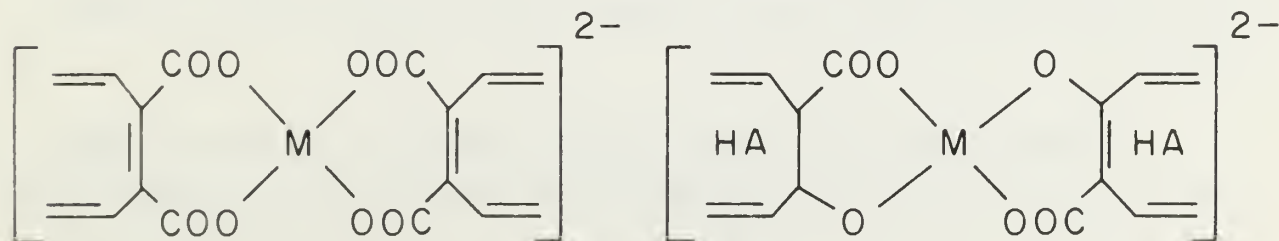
The research conducted thus far has led to the following speculations regarding the mechanisms of metal binding by humic acids:

1. Carboxyl groups play a prominent role in the binding of metal ions. Evidence in support of this conclusion is based on the observation that the binding capacity of humic acids for metal ions (e.g.,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) is essentially equivalent to one-half the number of titratable  $\text{H}^+$  ions, or an  $\text{M}^{2+}/2\text{HA}$  ratio of unity. Bonding may occur through two carboxyl groups or between a carboxyl and a phenolic hydroxyl group, as suggested by others in the literature. A substantial proportion of the carboxyl groups (two-thirds for the Leonardite humic acid) has been found to occupy positions such that cyclic anhydrides can be formed. Thus, one major complex may be of the phthalic acid type.

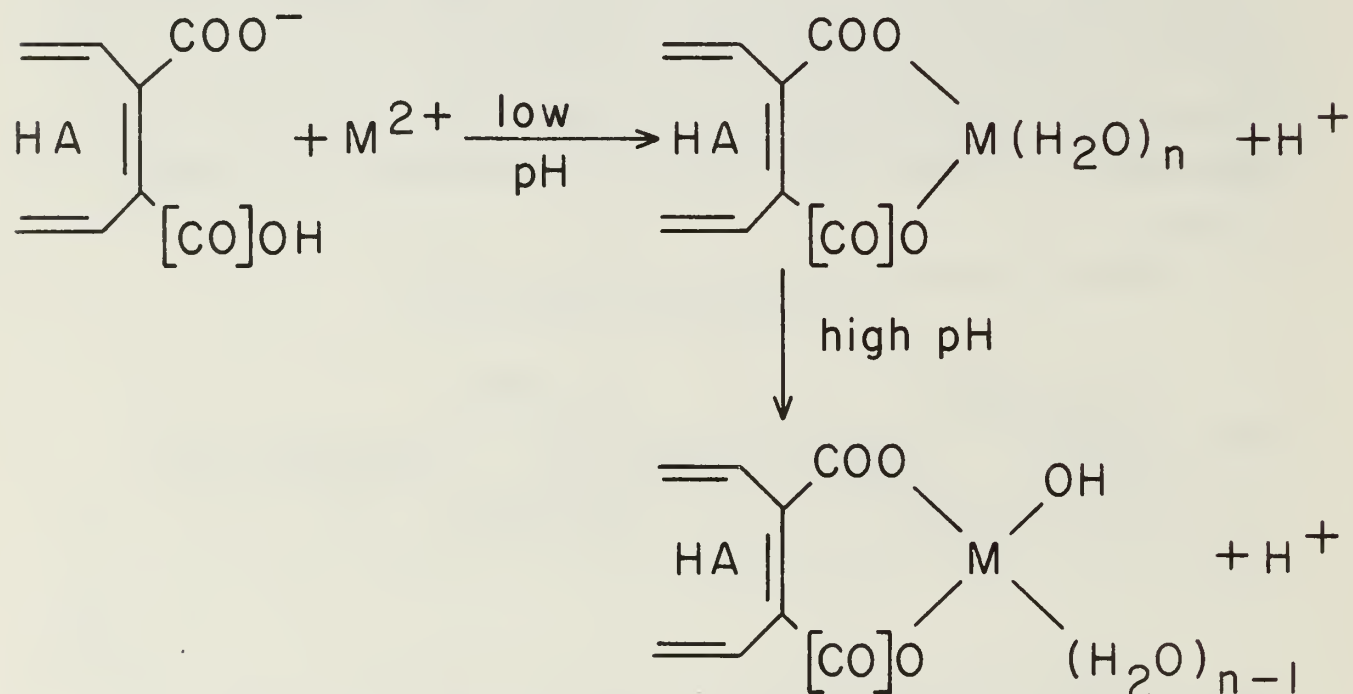
The basic reaction can be illustrated as follows:



2. Initially, 2:1 complexes are formed simultaneously to 1:1 complexes. These are probably of a mixed type, as suggested in (1). Because of structural considerations, 2:1 complexes are unlikely to be formed within the same molecule, but the metal serves to link individual molecules together to produce chain-like structures, as follows:



3. At low pH values, the drop in pH upon addition of the metal ion results from enhanced ionization of participating acidic groups (see 1). However, as the pH is increased, protons are also dissociated from hydration water of the metal held in 1:1 complexes. This conclusion is in agreement with van Dijk's theory and is based on the observation that the pH at which extra protons are released follows the order at which metal oxide hydrates are formed. The reaction is:

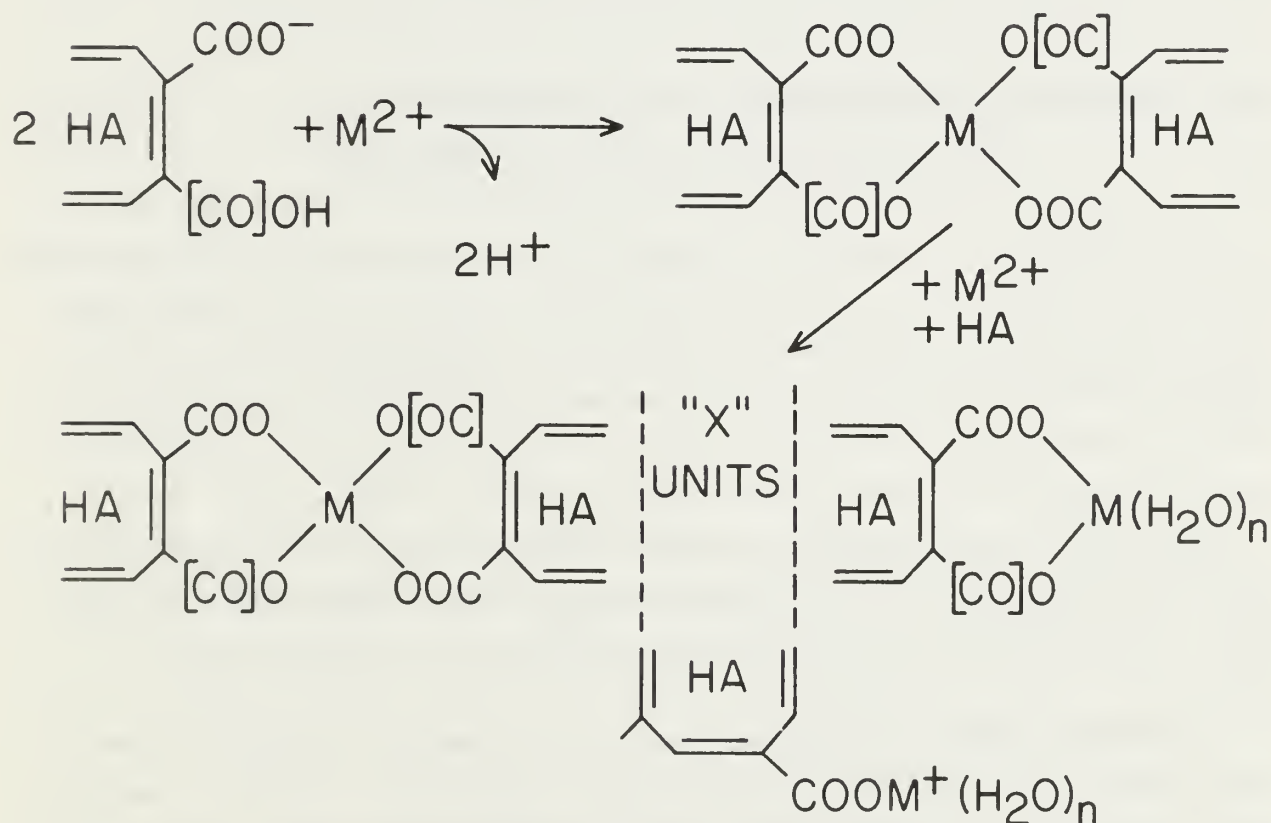


At low  $\text{M}^{2+}/\text{HA}$  ratios, horizontal displacement of the titration curves also results from release of  $\text{H}^+$  from an otherwise nontitratable acidic group. However, as the  $\text{Pb}/2\text{HA}$  ratio is increased, an increasing amount of the metal ion occurs in 1:1 complexes and the curves assume a flattened appearance. A further drop in pH results when precipitation takes place (see 2), apparently because of enhanced dissociation of hydration water from 1:1 complexes, as well as from metals held in salt linkages through isolated carboxyl groups (see 4).

4. Metal complexes of humic acid are soluble at low  $\text{M}^{2+}/2\text{HA}$  ratios (few combined molecules in the chain) but precipitation occurs as the chain-like structure grows and the isolated carboxyl groups become neutralized

through salt bridges. The point at which visible precipitation occurs was found to be influenced by such factors as ionic strength, pH, and humic acid concentration but most often occurred at a Pb/2HA ratio near 0.5.

The following diagram shows the metal ion: (a) as a 2:1 chelate complex holding two molecules together in a chain, (b) as a 1:1 complex at the end of a chain, and (c) in a salt-type linkage with an isolated carboxyl group.



Formation of 2:1 complexes of the type shown would result in a net charge on the molecule, thereby enhancing solubility.

5. Finally, the results of the research suggest that organic matter *per se* may not be as effective in binding  $\text{Pb}^{2+}$  as sometimes thought for the reason that the bulk of the organic matter in most soils is tightly bound to clay, probably as a clay-metal-organic matter complex. The results of the extraction studies show that any peripheral complexing sites would be occupied already by trivalent cations, such as  $\text{Fe}^{3+}$ . Although proof is lacking, it is suggested that it is the *newly formed humic substances* that form highly stable complexes with  $\text{Pb}^{2+}$  introduced into soil as a contaminant, according to the sequences described above. Ultimately, the  $\text{Pb}^{2+}$  could serve as a bridge between organic matter and clay, in which form it would be completely immobile and unavailable to plants and microorganisms. The possible formation of clay-lead-organic matter complexes deserves further study.

#### LEAD DEPOSITION AS AN AEROSOL AND ITS EFFECT ON PLANTS

##### Characteristics of Lead Aerosol Deposition

Lead aerosol was generated from lead chloride with a 1 to 3 micron particle size. This aerosol was introduced into a closed, 3 x 1 1/2 foot plexi-glass box with ports in the bottom through which the aerial portion of ten soybean plants could be placed and simultaneously fumigated. The aerosol was blown in from beneath the chamber with exit portals placed on either side. During fumigation the plants were irradiated with sufficient light intensity to cause full stomatal opening. In most experiments the plants were fumigated for a 12-to-15-hour period. In each experiment, particulate deposition was quite uniform both on leaves of the same plant and on different plants.

Aerosol deposition has been measured for leaves of several different plant species including sunflower, soybean, tulip poplar, basswood, and sycamore. Sunflower and soybean leaves have rough pubescent leaves whereas those of the latter 3 species are relatively smooth and glabrous. We have found the deposition velocity of the pubescent leaves to be 2 to 7 times that of the glabrous leaves. There was no significant difference in deposition velocity between species having pubescent leaves or between species having glabrous leaves. This finding indicates a good possibility for categorizing the particle-scavenging efficiency of different plant species according to their leaf surface characteristics.

Preliminary experiments have shown that increasing relative humidity results in an increase in the rate of deposition of aerosol particulate on plant leaves. We are now in the process of a detailed examination of the relationship between humidity and deposition for different particle sizes.

#### Movement of Lead from the Leaf Surface

Experiments were conducted to determine the within-plant translocation of topically applied lead as well as its effects on photosynthesis and transpiration. Leaves which were fumigated to approximately 1500 ppm showed very little lead movement from the fumigated leaves to newly formed leaves. In other experiments, the terminal bud was removed, causing the formation of axillary leaves immediately adjacent to the fumigated leaves. At fumigation levels of approximately 1500 ppm, very little movement of lead occurred from the fumigated leaves to the sink region of the new axillary leaves. When beans developed at four weeks after fumigation they were also analyzed for lead content. No significant concentrations of lead could be found in beans. Even when plants were fumigated at levels from 4000 to 6000 ppm, there was no substantial movement of lead from the fumigated leaves to the other parts of the plant.

The effect of rainwater washing in removing topically applied lead particulate from soybean plants has been determined. Deionized water falling 10 feet in droplet form from capillaries mounted at 1 inch centers in a plexiglass module was used to simulate rainfall. A height of 10 feet is sufficient for water droplets to attain a velocity equal to approximately 90% of that observed for natural rain drops. Under these conditions, 1 inch of rain was found to wash approximately 85% of recently deposited lead particles from the leaf surface. A one-inch rainfall seemed sufficient to wash off all the 85% of the total lead which could be removed from the leaf surface, no matter if the interval of rain was 15, 30 or 60 minutes. In addition, it was found that rainstorms of greater than 1 inch did not wash off any more than the 85% which was washed off by the initial one-inch rainstorm.



In an additional experiment we determined the relative importance of mechanical splashoff by raindrops vs. dissolution and subsequent runoff resulting from a misting treatment. During the rain treatments, raindrops landed on the leaf surface with a force which was sufficient to cause the raindrop to break up and the leaf to rebound from the impact. On the other hand, the much smaller droplets of the mist settled on the leaf surface and coalesced into larger drops which then ran toward the leaf edge and dropped off without causing very much leaf movement. The results of all precipitation experiments are similar in that the functional relationship between the amount of lead remaining on the leaf and the duration of precipitation were the same, i.e., the data for each experiment conform to a  $y = ax^b$  relationship where y represents the amount of lead left on the foliage and x represents the amount of precipitation. However, the misting treatment removed a slightly greater percentage of the lead at each value of precipitation than either of the rain treatments. This indicates that dissolution may be an important mechanism in removal of  $PbCl_2$  from the surfaces of leaves. If the rain treatments had removed more lead than the mist it would have indicated that another mechanism, that of bombardment and splashoff, would have been the predominant mechanism for particulate removal.

#### Effect of Aerosol-Deposited Lead on Plant Gas Exchange Processes

In leaves fumigated to 1500 ppm, no substantial reduction in photosynthesis, as measured by gas exchange, was noted subsequent to treatment. This indicates that stomates were not blocked by the deposition of lead at these particle sizes and concentrations.

In other experiments, soybean plants were fumigated with 1500 ppm lead and subsequently exposed to wind regimes at 5, 10 and 15 mph. In no instance was there significant reentrainment of deposited lead from the leaf surface into the air stream, even though the leaves were in fairly violent motion during the wind treatment.

## EFFECTS OF ENVIRONMENTAL FACTORS ON LEAD AND CADMIUM EFFECTS ON PLANTS

### Soil Variables

#### Lead and Cadmium Interactions

The interactive effects of lead and cadmium on corn root growth was investigated by Hassett, Miller, and Koeppe<sup>7</sup>. It was found that radicle elongation of soil-grown corn seedlings was depressed by concentrations of 25  $\mu\text{g}$  Cd/g of soil or 250  $\mu\text{g}$  Pb/g of soil when the metals were added singly. When lead and cadmium were added in combination, inhibition of radicle elongation occurred at significantly lower concentrations. The effect of the metals when added in combination was greater than the sum of effects when the metals were added singly, thus strongly suggesting a synergistic interaction. The effect was partially attributed to elevated accumulation of metals in the combination treatments.

A Bloomfield loamy sand was treated in a related experiment with different levels of lead and cadmium<sup>8</sup>. The effect of lead and cadmium on corn growth, the effect of lead on cadmium uptake, and the effect of cadmium on lead uptake by the corn plants were determined for four different time periods. Increasing cadmium levels in the soil result in decreased lead uptake; total lead in the corn as well as the concentration of lead in the corn decreased as cadmium levels in the soil increased.

Both the total amount and the concentration of cadmium in the corn plants increased as soil lead levels increased. The intermediate soil lead levels resulted in the greatest increase in lead uptake, but all soil lead levels increased the cadmium uptake over that in the controls.

In a study of sycamore seedlings, Bazzaz and Carlson examined the response of sycamore growth, photosynthesis, and transpiration to different soil concentrations of lead and cadmium alone as well as the two metals together.

Root growth was found to be synergistically affected by the lead-cadmium treatment. New stem growth, diameter increment, and photosynthesis were reduced more by the combined lead-cadmium treatment than by either heavy metal alone but not enough to be considered a synergistic response. Heavy metal accumulation by plant parts increased with higher treatment levels but was much lower than values previously reported in the literature.

#### Interaction of Cadmium Effects with the Effects of Drought Stress

Experiments have been conducted using polyethylene glycol, as well as natural drying conditions, to determine if drought stress affects the uptake of cadmium and its subsequent effect on plant processes. In all experiments to date, it has been found that with increasing drought stress there is less cadmium taken up into the leaves of three- to four-week-old corn plants. It is hypothesized that the reason for reduced cadmium uptake into the tops of corn is the slowing of the transpirational stream under conditions of drought stress.

#### Interactions between Lead and Soil Microorganisms

##### Effect of Lead on Soil Biological Activity

The approach used in this study was to examine the effect of lead upon enzyme synthesis when the appropriate substrate is added to soil. The rationale of this approach is that protein synthesis, by virtue of its dependence (1) upon the multiple requirements for metabolically active cells, (2) upon abundant energy and precursors, and (3) upon availability of inorganic nutrients from which precursors are synthesized (e.g., nitrogen and phosphorus), would be a sensitive measure of disruption of a variety of microbial processes. That is, if lead destroys cells or inhibits any catabolic or anabolic reaction required for protein synthesis, the observed result would be a decreased rate of enzyme synthesis. In addition, a good correlation between soil enzyme levels and microbial numbers has been reported in several cases.



The results obtained (Table 2) indicated that lead was a potent inhibitor of amylase and  $\alpha$ -glucosidase synthesis but had little effect upon invertase synthesis.

In parallel with the amylase assays, numbers of amylase-producing bacteria were determined and the average level of lead resistance of these bacteria was examined. Numbers of amylase-producing bacteria declined in parallel with the decline in amylase activity in soil during the interval from 25 to 72 hours and rose at 96 hours. The parallel decline in bacterial numbers and amylase activity indicates that the major effect of lead addition was to kill amylase-producing cells.

Table 2  
Enzyme Synthesis in Lead-Amended Soil\*

Time (hours)	SPECIFIC ACTIVITY†					
	Amylase		$\alpha$ -glucosidase		Invertase	
	-Pb	+Pb	-Pb	+Pb	-Pb	+Pb
0	0.2	0.2	2.3	1.9	0.3	0.2
4	0.2	0.2	2.1	1.7	1.0	1.9
24	2.8	3.3	10.6	10.1	2.1	2.4
25	2.6	3.0	10.6	2.5	2.1	1.5
48	3.9	2.1	8.6	4.3	2.7	2.7
72	3.8	2.0	6.2	4.3	2.7	2.3
96	4.9	4.7	3.9	4.7	2.0	2.6

\* Samples of Drummer soil (100g) were amended with 1 g starch (for amylase induction), maltose ( $\alpha$ -glucosidase), or sucrose (invertase) at  $t = 0$  and incubated at 25°C. At 24 hours, lead acetate (1.1 g) was added to samples designated "+Pb", while no lead acetate was added to samples designated "-Pb". Aliquots of soil were assayed for the appropriate enzyme at the times indicated in the table.

† Specific activity is defined as  $\mu$ moles of product formed/g of soil/unit of time.

The increase in bacterial numbers and amylase activity at 96 hours could be explained by immobilization of lead, followed either by increased microbial growth or by an increase in the numbers of lead-resistant amylase-producing bacteria. The data presented in Tables 3 and 4 indicate that lead levels did not decrease, while the abundance of lead resistant bacteria increased. The distribution of lead-resistant bacteria did not change over time in samples to which no lead was added. Therefore, the recovery of amylase synthesis may be attributed to a change in the nature of the soil population, with lead-sensitive amylase producers being the major amylase producers prior to lead addition, and lead-resistant amylase producers being the major amylase producers after lead addition.

Table 3  
Soluble Lead Levels in Enzyme Assays

Lead Salt Added*	Soluble Lead Levels**	
	t = 0 <sup>†</sup>	t = 48
Pb acetate	7.9 <sup>**</sup>	7.9
PbCl <sub>2</sub>	6.8	5.6
PbSO <sub>4</sub>	10.5	10.1
PbS	2.6	2.6
None	<0.8	<0.8

\* All were added to give 1800 ppm Pb<sup>2+</sup>/g of soil (see Table 5 for amylase levels in these samples).

\*\*Values are ppm Pb<sup>2+</sup> soluble in 0.1 M acetate buffer, pH 5.5.

<sup>†</sup> t = time in hours after addition of lead to soil.

Table 4

Average Level of Lead Resistance of Soil Bacteria  
Prior to and Following Addition of Lead Acetate to Soil\*

Time <sup>†</sup>	Number of Isolates Resistant to:			
	<250 µg/ml Pb	>250, <500 µg	>500, <1000 µg	>1000, <2000 µg
24 hour	3	8	28	46
25 hour	0	3	53	40
48 hour	1	0	43	47
120 hour	0	0	58	39

\* Samples from which isolates were selected were treated as described in Table 2.

<sup>†</sup> Lead acetate was added immediately after taking the 24 hour sample.

The data in Table 5 indicate clearly that the decline in amylase and  $\alpha$ -glucosidase activity is the result of inhibition of enzyme synthesis, not inhibition of enzyme activity.

Further experiments with amylase synthesis were conducted using lead salts of different solubilities (Table 6). The influence of lead oxide (PbO) and lead sulfate upon amylase synthesis was also tested; PbO did not inhibit synthesis at 13.0 mg Pb<sup>2+</sup>/g of soil, while PbSO<sub>4</sub> reduced amylase synthesis to 35% of control (-Pb<sup>2+</sup>) levels when added at 10.2 mg Pb<sup>2+</sup>/g of soil.

It is evident from these results that no clear relationship exists between lead solubility and inhibition of enzyme synthesis, since the least soluble lead salt (PbS) was more inhibitory than the more soluble PbO and PbSO<sub>4</sub>.

Table 5  
Comparative Inhibition of Enzyme Synthesis and  
Activity by Lead Acetate

Pb <sup>2+</sup> , mg/g Soil	Amylase		$\alpha$ -glucosidase	
	Activity*	Synthesis <sup>†</sup>	Activity*	Synthesis <sup>†</sup>
0	1.0	1.0	1.0	1.0
2	0.88	0.26	0.96	0.63
4	0.84	0.16	0.95	0.42
8	0.72	0.10	0.98	0.23
12	0.55	0.08	0.77	0.19

\* Lead acetate was added to the assay mixtures after a 24 hour induction period. Activity is expressed relative to enzyme levels in the absence of lead.

<sup>†</sup> Lead acetate was added to soil at t = 0 as described in Table 6 and soil enzyme levels were determined at t = 24. The amount of enzyme synthesized is expressed relative to the amount synthesized in the absence of lead.

Table 6

Comparative Inhibition of Amylase Synthesis by Lead  
Acetate, Chloride, and Sulfide

Lead Concentration ( $\mu\text{g/g}$ soil)	Amylase Specific Activity*		
	<u>Lead Source Added</u>		
	Pb Acetate	$\text{PbCl}_2$	PbS
<u>24 Hours After Lead Addition</u>			
0	2.02 + 0.57*		
450	0.72 $\pm$ 0.15	1.97 $\pm$ 0.31	1.64 $\pm$ 0.45
900	0.62 $\pm$ 0.05	1.24 $\pm$ 0.24	1.50 $\pm$ 0.23
1800	0.52 $\pm$ 0.03	0.61 $\pm$ 0.08	0.89 $\pm$ 0.03
1800	0.44 $\pm$ 0.03	0.49 $\pm$ 0.04	0.73 $\pm$ 0.06
<u>48 Hours After Lead Addition</u>			
0	3.89 $\pm$ 0.57		
450	3.21 $\pm$ 1.28	5.53 $\pm$ 0.67	2.95 $\pm$ 0.39
900	2.72 $\pm$ 0.76	3.11 $\pm$ 0.86	4.95 $\pm$ 0.44
1800	1.92 $\pm$ 0.42	0.96 $\pm$ 0.06	2.33 $\pm$ 0.70
1800	1.84 $\pm$ 0.38	0.93 $\pm$ 0.14	1.66 $\pm$ 0.33

\* Soils were amended with 1 g starch or maltose/100g of soil and the indicated lead salt at  $t = 0$ . At  $t = 24$  and 48 hours, enzyme assays were performed. Values given are the mean activity  $\pm$  standard deviation; 6 samples were averaged for each value given.

The data demonstrate that lead can be a potent inhibitor of soil biological activity, but that this inhibition is selective and is not dependent solely upon the water solubility of the chemical form in which lead is added to soil.

#### Solubilization of Lead Salts by Soil Bacteria

A number of soil bacteria have been isolated which are able to convert insoluble lead salts into a soluble form. The data presented in Tables 7 and 8 demonstrate that solubilization is a complex phenomenon involving interactions between the specific organism, the lead salt used, and the nutrients available. The observed transfer of lead from the tubing to the surrounding medium did not occur unless the medium was inoculated. For a particular isolate the transfer was dependent upon the composition of the medium. For example, compare the amount of lead mobilized by isolate 8a grown in nutrient broth with the amount solubilized in nutrient broth + glucose. Movement of PbS was also observed in solid media where cells were separated from PbS by a Pb-free agar layer 10 mm thick. The mobilization of PbS only in media of specific composition and with two different culture conditions (liquid and solid) indicates that this movement of PbS was not a purely abiotic phenomenon but requires microbial activity.

The ability of these isolates to enhance lead uptake by corn growing in PbS-amended sand is currently being examined; no data are available at this time.

#### Prediction of Effect of Soil Lead on Microbial Activity and Plant Yield

Because of (1) the rapid binding of lead to soil components, (2) the reported lack of inhibition by lead of bacterial growth in culture, and (3) the low solubility of most lead salts, it was initially hypothesized that lead would have little, if any, effect upon soil biological activity. Consequently, it appeared likely that the research described earlier in this section would be of limited duration and would yield results consistent with data obtained in experiments where the effect of lead upon plant growth was examined. The data in Tables 2, 4, and 6 indicate that lead in soil *does* affect microbial activity.



Table 7  
Solubilization of  $\text{PbSO}_4$ ,  $\text{PbS}$ ,  $\text{PbCO}_3$ ,  $\text{PbO}$ , and  
 $\text{Pb}_3\text{O}_4$  by Soil Bacteria in Culture\*

Lead Salt	Organism	$\mu\text{g Pb/Flask Outside Dialysis Tube}^\dagger$					
		Nutrient Broth			Nutrient Broth + Glucose		
		Soluble Pb	Cell Pb	Total Mobilized	Soluble Pb	Cell Pb	Total Mobilized
PbS	1	50	6370	6420	30	190	220
	8a	100	5485	5585	20	25	45
	4a	50	455	505	130	2435	2565
	7c	30	5	35	30	635	665
	8b	110	1385	1495	0	85	85
	5c	100	1835	1935	320	3485	3805
$\text{PbSO}_4$	1	<30	<30	-	0	5	5
	8a	<100	890	<990	5	0	5
	4a	<20	<15	-	0	0	0
	7c	<30	<80	-	0	15	15
	8b	0	5	5	10	55	65
	5c	0	0	0	40	30	70
$\text{PbCO}_3$	1, 8a, 4a						
	7c	0	0	0	0	0	0
	8b	10	0	10	30	3375	3405
	5c	30	0	30	30	0	30
PbO	1, 4a, 7c, 8b, 5c	0	0	0	0	0	0
	8a	0	160	160	0	0	0
$\text{Pb}_3\text{O}_4$	1	0	0	0	0	80	80
	4a, 7c, 8b, 5c	0	0	0	0	0	0

\* Cells were grown for 48 hours in flasks containing either nutrient broth or nutrient broth + 0.5% glucose. Lead sulfide (25 mg Pb/flask) was enclosed in dialysis tubing, which was immersed in the culture medium. Flasks were incubated at 32° C with shaking. After 48 hours, samples of cell-free culture medium and cells were digested in 50% (v/v)  $\text{HNO}_3$  and lead was determined by atomic absorption spectrometry.

† Values for uninoculated flasks have been subtracted.

Table 8

Influence of Medium Composition upon Solubilization of PbS

Addition to Basal Medium*	Amount of Pb Outside Dialysis Bag Organism <sup>†</sup>					
	1	7c	8b	5c	8a	3
Tryptone, 0.05 mg/ml	--	-	--	+++	--	-
Tryptone, 1 mg/ml	--	-	++	++	++	-
Nutrient broth	++	+	--	--	++	-

\* Basal medium contained (in g/l): glucose, 5; Tris buffer, 1.3; sodium phosphate, 0.2; magnesium sulfate, 0.02; and calcium chloride, 0.004. PbS was enclosed within dialysis tubing as described in Table 2.

<sup>†</sup> Code: observations range from --, no PbS visible outside tubing, to +++, medium was dark grey because of suspended PbS in medium.

The fact that lead has an effect indicates that a more thorough examination of the influence of lead upon microbial decomposition of organic molecules is necessary before the information can be used for predictive purposes. Decreased decomposition of organic residues could have several important effects upon crop yields on a long-term basis, including: (1) reduced availability of nitrogen and carbon (CO<sub>2</sub>) for recycling into subsequent crops, (2) increased availability of substrates for lead-resistant organisms, some of which may be plant pathogens, and (3) potential reduction in the ability of soil organisms to detoxify pesticides, thereby increasing their residence times in soil. In the case of herbicides, persistence could result in yield reductions when herbicide-sensitive crops follow herbicide-resistant crops in a normal rotation program.



### III. URBAN DUST STUDIES

The Urban Dust Group has concentrated its research efforts during the past year on two areas: (1) surveying the distribution of lead and cadmium in urban dusts and soils, and (2) investigating the sources, transport mechanisms, and physical and chemical characteristics of particles containing lead, cadmium, and polycyclic organic molecules (POM).

#### LEAD DISTRIBUTION STUDIES

This section presents the results of an area-wide survey of lead and, to a lesser extent, cadmium in settled dusts and soils in the small urban community of Champaign-Urbana, Illinois (population 100,000). Indoor and outdoor samples (approximately 1400) were taken in residential and nonresidential areas. It was desired to measure trace metal levels, especially lead, which offer a risk to children in a "best world" situation rather than in decaying neighborhoods. The homes selected were in good repair, painted with nonleaded or low-lead paints, and were located in relatively low traffic density areas. Measurements were also made in nonresidential locations such as schools, streets, and offices. What has emerged is a picture of lead and cadmium being present everywhere--in homes, schools, offices, and streets--in unexpectedly large amounts.

#### Review of Experimental Techniques

Settled dusts were gathered by a vacuuming technique using a special nylon filter holder. A glass-fiber paper (Gelman Type A) insert was used in each sampling run. A portable pump provided the vacuum source. The vacuumed dust is trapped in the upper chamber of the nylon holder. The used filter and the dust gathered were placed in tared glassene envelopes. Glassene envelopes and clean filters were humidity and temperature equilibrated for 24 hours before initial and final weighings. When weighings were made or dusts handled, plastic gloves were worn to prevent contamination of samples.

Each sample was collected from within a 0.5 m x 0.5 m wood template, as shown in Figure 2, allowing results to be reported on an area basis ( $\mu\text{g Pb/m}^2$ ) as well as on a weight basis ( $\mu\text{g Pb/g dust}$  or ppm). Indoor samples were always taken in the central area of a room, away from the walls.

One pass with the special vacuum holder was made in each  $0.25 \text{ m}^2$  sample area. The error in the weight fraction of lead resulting from making only one sweep was determined to be less than 6%.

Soil samples were taken with a standard soil borer. The top 2.5 cm of soil was sampled.

Analyses for lead and cadmium were carried out by atomic absorption spectrometry. Analysis of the data from duplicate samples using the t-test indicated no significant difference of the pair means either on a weight or area basis at a 95% confidence level. Confidence level on the data is  $\pm 20\%$  including analytical and sampling factors.

## Results

### Interior Residential

A total of 239 floor-dust samples were taken in twelve homes. Four of the homes were sampled twice. Ten of the homes were single-family residences and two were located in multistory apartment buildings (sites F and K). A summary of the indoor residential lead and cadmium data is shown in Table 9. For the twelve homes, average indoor lead levels of 600 ppm and  $680 \mu\text{g/m}^2$  were found. All of the homes were upper-middle-class abodes in extremely fine condition with no paint chipping or peeling. It would seem that a substantial fraction of the very high lead levels must be the result of lead settling from automobile emissions. Cadmium levels were also quite high as discussed below.



Figure 2. Dust sampling procedure.

Table 9  
Mean Lead and Cadmium Levels in  
Settled Floor Dusts at Residential Sites

Site Code	Lead		Cadmium	
	ppm	$\mu\text{g}/\text{m}^2$	ppm	$\mu\text{g}/\text{m}^2$
A	1440	1180	28	26
B	690	710	19	14
C	940	1700	10	31
D	760	580	10	11
E	900	1590	20	37
F	350	760	48	132
G	240	100	26	7
H	500	70	25	3
I	170	120	7	4
J	270	400	9	15
K	430	650	12	15
L	460	220	12	6
Average, 12 Sites	600	680	18	25

Detailed results for individual homes have been tabulated for rug-covered surfaces and non-rug-covered surfaces in Table 10. The lead content of dust found on non-rug-covered surfaces (wood or tile) is generally higher than that found on rugs: 950 ppm lead versus 450 ppm lead on the average. However, the total amount of settled lead (as measured on an area basis) is higher on rugs; i.e., there is more dust accumulation on rugs than on bare floors.

Cadmium contents as high as 105 ppm and  $219 \mu\text{g}/\text{m}^2$  were measured in some homes. On rugs, extremely large amounts of cadmium are found-- $44 \mu\text{g}/\text{m}^2$  on the average. This high level is probably caused by the rubber backing found on many carpets. A random sample of this material assayed 3000 ppm cadmium. Abrasion would account for the cadmium being present in dust.

Ventilation patterns, number of pets, and number of inhabitants as well as airborne lead levels can be expected to influence the dust lead levels. Lead levels in outdoor air were measured<sup>9</sup> over a long period of time at eight of the twelve sites (A, B, C, D, E, G, H, L) and fairly close to two others (H, J). Although outdoor airborne lead levels were low, with a mean of  $0.28 \mu\text{g}/\text{m}^3$  and a range from 0.18 to  $0.34 \mu\text{g}/\text{m}^3$ , in general, the sites with the highest outdoor airborne lead had the highest settled dust lead levels. The magnitudes of the lead dust levels are similar to those found by Kreuger<sup>10</sup> in suburban dust near Boston.

#### Interior Nonresidential

For a more complete picture of human exposure it is desirable to know the level of lead and cadmium in dust in locations where people work, visit, and shop outside the home. Presumably, adults inadvertently carry dust on their clothes and shoes from these areas back into the home where it becomes available for infant/child ingestion.

Over 350 samples were taken in university laboratories and classrooms, schools, hospitals, and food markets. Detailed results are shown in Table 11.

Table 10

Lead and Cadmium Content of Floor Dust in Homes  
(Rug-Covered versus Non-Rug-Covered Surfaces)

Site Code		Number of Samples	Lead		Cadmium	
			ppm	$\mu\text{g}/\text{m}^2$	ppm	$\mu\text{g}/\text{m}^2$
A	Rugs	7	830	1490	24	43
	Non-rugs	13	1780	1020	29	17
B	Rugs	7	550	590	16	18
	Non-rugs	6	1440	1980	13	18
B (repeat)	Rugs	5	420	460	17	20
	Non-rugs	10	480	140	25	6
C	Rugs	14	640	2710	14	58
	Non-rugs	9	770	360	7	4
C (repeat)	Rugs	14	520	1940	10	34
	Non-rugs	7	2580	930	7	5
D	Rugs	5	380	860	14	31
	Non-rugs	17	870	510	9	5
E	Rugs	8	340	3060	16	75
	Non-rugs	11	900	970	14	13
E (repeat)	Rugs	8	590	1110	12	20
	Non-rugs	9	1690	1490	36	46
F	Rugs	7	470	1320	64	219
	Non-rugs	1	250	40	2	4
F (repeat)	Rugs	6	240	350	66	71
	Non-rugs	1	290	60	105	22
G	Rugs	11	220	110	14	7
	Non-rugs	3	320	70	71	8
H	Rugs	1	300	170	11	6
	Non-rugs	4	550	40	28	2
I	Rugs	13	210	160	7	6
	Non-rugs	6	100	20	6	1
J	Rugs	7	370	800	13	30
	Non-rugs	8	190	40	4	1
K	Rugs	4	580	1160	13	26
	Non-rugs	4	270	140	10	4
L	Rugs	3	440	640	13	20
	Non-rugs	10	470	90	12	2
	All Rugs	120	450	1220	19	44
	All Non-rugs	119	950	600	18	10



Table 11

## Lead and Cadmium in Indoor Floor Dusts at Nonresidential Sites

Sampling Site	Number of Samples	Lead ppm $\mu\text{g}/\text{m}^2$		Cadmium ppm $\mu\text{g}/\text{m}^2$	
<u>Halls/Corridors</u>					
Roger Adams Lab	31	2720	690	14	6
Mech. Eng. Bldg.	36	3380	3010	9	8
Krannert Ct.	11	500	1190	7	21
Federal Bldgs.					
-Rugs	1	1710	18000	23	240
-Non-rugs	2	4680	360	369	28
Krannert Garage	10	1830	8650	5	25
Columbia Sch.	4	1010	1640	9	15
Gregory Hall	3	740	230	5	1
<u>Rooms in University Bldgs.</u>					
University Labs					
-299 RAL	35	11400	3390	185	57
-221 RAL	18	6280	5770	86	74
-57-59 RAL	8	910	120	33	4
-136-138 RAL	7	5740	3560	69	34
-11 RAL	9	8060	26560	79	302
University Offices					
-105, 115, 116, -202, 222 RAL	11	1450	640	13	7
University Classrooms					
-Variou s - Gregory Hall	7	590	190	24	3
-Variou s - Lincoln Hall	8	930	155	1	0
<u>Rooms in Other Bldgs.</u>					
Federal Bldg. Offices					
-Rugs	6	2320	11780	1033	2943
-Non-rugs	1	2960	560	1060	200
Columbia Sch. Classes					
-Rugs/Mats	10	730	3990	29	122
-Non-rugs	17	650	200	7	4
All Floors	27	680	1600	15	48
Dr. Howard Sch. Classrooms					
-Rugs/Mats	12	410	2360	30	115
-Non-rugs	26	430	210	19	5
All Floors	38	420	890	23	71
Carle Hosp. Complex					
Entry Areas (carpet)	11	620	7940	20	390
Hosp. Corridors/Rooms	11	360	180	22	4
Food Markets					
Plain floors	34	490	100	9	2
Matted areas	2	730	18000	24	290

Lead levels in corridor dust are about as high as in interior rooms. Extremely large amounts of lead and cadmium are found everywhere, ranging from 500 to 3000 ppm lead and 1 to 50 ppm cadmium. As in residences, high total cadmium levels are associated with rubber mats or rubber-backed carpeting.

Astonishingly high levels of lead and cadmium are found in chemical laboratories. Paint chipping was not observed in any of the laboratories (or indeed in any of the other locations sampled). Since lead and cadmium levels in offices adjacent to the laboratories are much lower, some of the trace metals in the laboratory dust are probably of local chemical origin.

Average levels of lead and cadmium for the nonresidential survey, excluding chemical laboratories, are shown in Table 12.

Levels of lead and cadmium are nearly twice residential averages. In the case of lead, this difference reflects the magnitude of outdoor airborne lead levels in the nonresidential areas (two to five times residential averages).

### Outdoor Residential

Outdoor lead and cadmium were measured in the soils and dusts surrounding the 10 one-family residences of the indoor study. Eight of the homes were painted frame houses while the other two had painted trim. All are in low-traffic-density areas. Paint samples from 8 of the homes have been analyzed to date. They assay <1% lead and <50 ppm cadmium. All of the homes were in good condition with no evidence of paint peeling or chipping.

All of the 288 soil and dust samples taken were analyzed for lead and 177 were analyzed for cadmium. In Figure 3, the data have been grouped by areas around a typical house in a composite. Medians and range of data are shown. Near is defined as  $\leq 1$  meter.

Lead levels in dusts are very high both near the road and near the house. The range in dust lead content is 240 to 6640 ppm away from the house and 130 to 11,760 ppm near the house.



Table 12  
Mean Lead and Cadmium Levels in  
Settled Floor Dusts at Nonresidential Sites

Surface	Number of Samples	Lead		Cadmium	
		ppm	$\mu\text{g}/\text{m}^2$	ppm	$\mu\text{g}/\text{m}^2$
Rugs/Mats	42	860	6670	70	604
Non-Rugs/Mats	212	1500	1120	19	12
All Floors	254	1400	2040	44	110

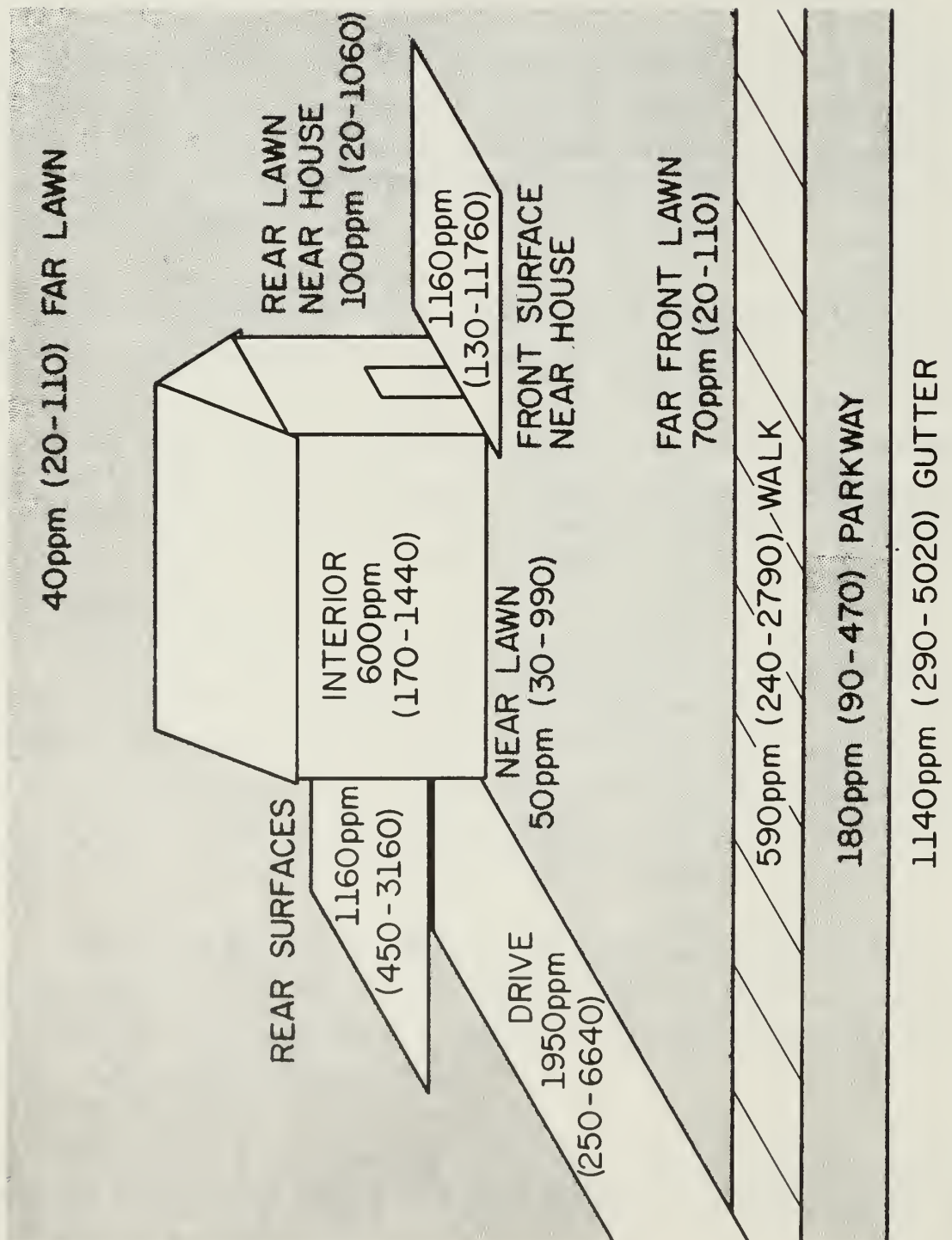


Figure 3. Composite lead in dust and soils in residential areas (median and range).

Soil lead levels are somewhat higher both near the road and house, but there is not a great deal of variation in soil lead concentrations. Soil lead values fall in the range from 20 to 1060 ppm.

Presumably, high lead content in soils and dusts adjacent to roadways results from auto emissions or reentrainment of settled dusts. High lead levels adjacent to the house would result from both paint weathering and from leaching and washoff of settled airborne automotive lead on the roof and window sills.

Lead levels are very high everywhere in the vicinity of the home, not only immediately adjacent to the exterior of the house. It seems unreasonable, therefore, to ascribe all the lead and all the danger to paint. Children spend very little time immediately adjacent to the side of a typical home.

The net amount of lead found in the home areas was surprisingly large. The amount was largest in gutters, with a median value of  $21,300 \mu\text{g}/\text{m}^2$  and a range from 1270 to  $211,000 \mu\text{g}/\text{m}^2$ . In driveways the median value was  $5820 \mu\text{g}/\text{m}^2$  with a range from 1050 to  $86,000 \mu\text{g}/\text{m}^2$ . On walks the median was  $1590 \mu\text{g}/\text{m}^2$  with a range from 720 to  $15,200 \mu\text{g}/\text{m}^2$ . On surfaces adjacent to the house the median lead content of dust was  $1840 \mu\text{g}/\text{m}^2$  with a range from 200 to  $9100 \mu\text{g}/\text{m}^2$ .

Cadmium levels, by weight, were somewhat higher in soils and dusts near the house (1 ppm Cd in soils, 6-8 ppm in dusts). Total cadmium dust levels were relatively uniform everywhere, ranging from 7 to  $20 \mu\text{g}/\text{m}^2$ .

The ten homes studied represent an ideal situation: there is relatively low traffic in the vicinity, low or nonleaded paints have been used, and the maintenance has been good. If homes which do not meet these conditions are studied, soil lead levels are found to increase dramatically.

A special study was made of seven other frame houses. All were painted with an identical type of high-lead paint (27% Pb by weight). The houses

were located in areas of higher traffic density with airborne lead levels 2 to 3 times higher than in the residential areas. Soil lead levels are shown in Figure 4 as the curve labeled residential. The houses are not presently used as personal residences, although they were so used in the past.

Soil lead levels are much higher in the vicinity of these seven houses as compared to the ten residences previously studied. The largest increases are in the very high soil lead found adjacent to the curb and adjacent to the house. However, these maximum soil lead values are of the same order of magnitude as the lead content of the settled dusts found in the walks and driveways of the ten houses painted with low-lead paints (see Figure 3). Thus, lead paint use is not the sole indicator of high settled lead concentrations.

#### Outdoor Nonresidential

A survey of lead and cadmium in outdoor dusts and soils was made in many of the same nonresidential locations used in the indoor survey. All buildings were of stone or brick construction. Dusts were sampled at seven sites (195 samples) and soils at 20 sites (183 samples). All samples were analyzed for lead and 70% for cadmium. The lead content of settled dusts as a function of distance from a road is shown in Figure 5.

As the figure shows, both the lead content of the dusts by weight and the total lead accumulation fall off with distance from the road. The roads in question all had traffic flows in the range from 5000 to 20,000 cars per day. Mean accumulations as high as  $190,000 \mu\text{g Pb/m}^2$  were measured on the sidewalk. Dust lead contents were about twice those in residential areas. No lead increase adjacent to the buildings was noted in the dust measurements. However, at only two sites could one take undisturbed dust samples near the building line.

The mean soil lead transect for these stone and brick buildings is shown in Figure 4. Soil lead levels are high near the road and decrease with distance from the road but then increase to the highest level adjacent to the stone buildings. The latter increase is possibly due to leaching of window trim paint, but more likely is due to washoff from roofs or ledges of settled lead from sources other than paint.

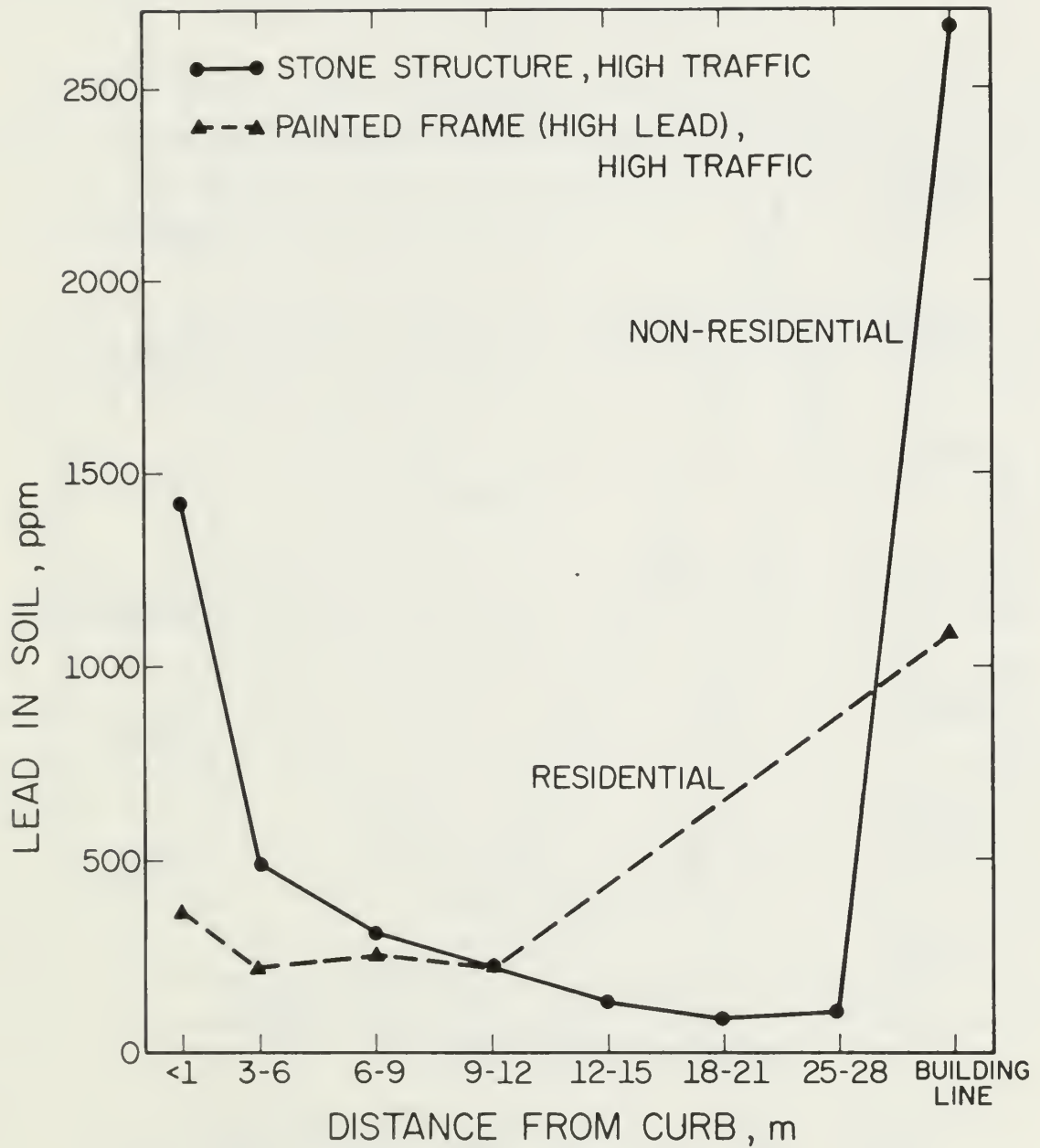


Figure 4. Mean lead in soils in high-traffic-density sites--residential and nonresidential.

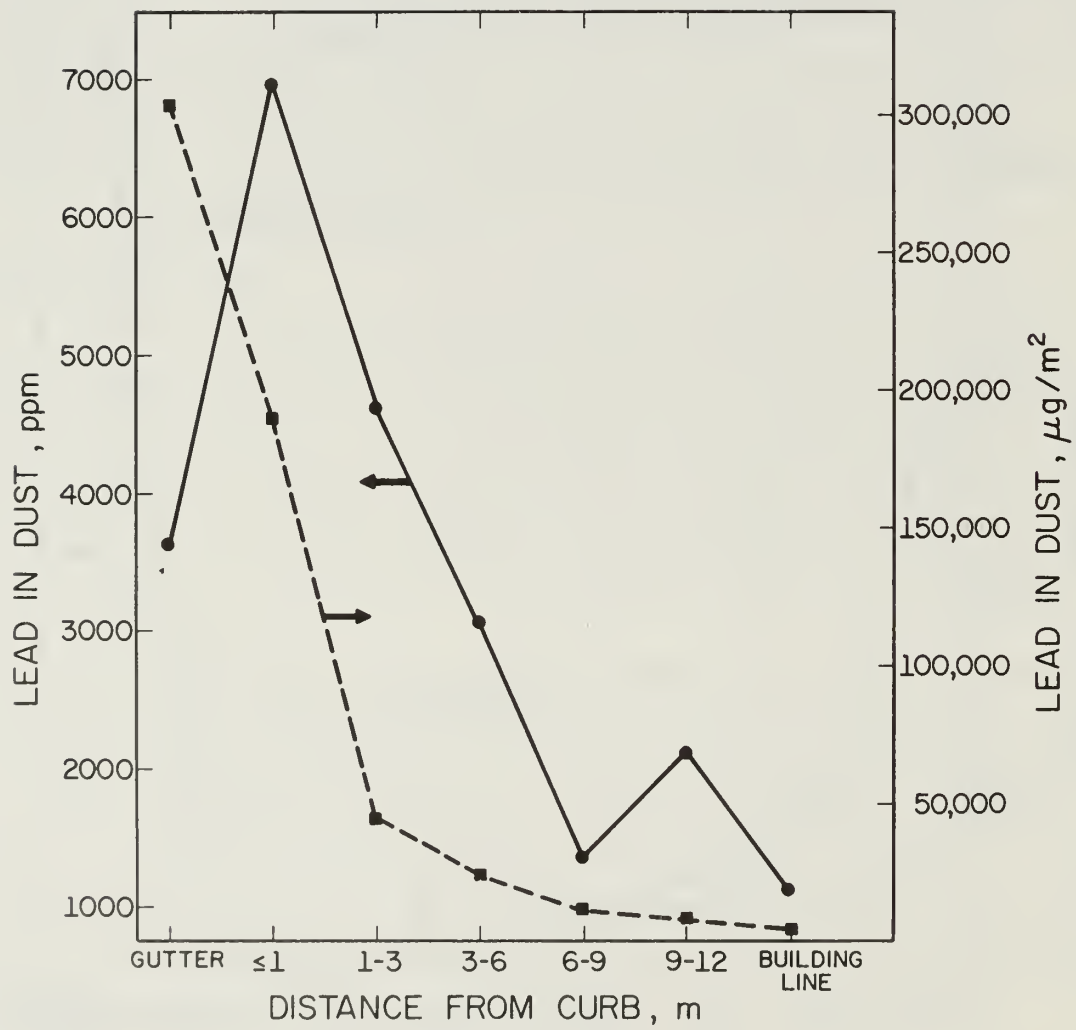


Figure 5. Mean lead in dust--nonresidential sites.



Soil lead contents are several times higher than normal residential values because of higher vehicular traffic in the area. As shown in Figure 4, curb soil values are also higher than those found in the special study of the seven homes painted with high-lead paint. Again, these high values are due to the even higher traffic levels in the nonresidential case.

However, the soil lead contents near the stone and brick building lines are higher than those found adjacent to the frame houses painted with high-lead paint. This fact strongly suggests that settled lead of airborne origin washes off of building surfaces and enters the soil.

Cadmium levels average 1 ppm in soils and from 2 to 6 ppm in dusts. No trends are discernable. Total cadmium in dust decreases from 134  $\mu\text{g Cd/m}^2$  to 1  $\mu\text{g Cd/m}^2$  near the building line.

### Discussion

Extremely large amounts of lead and cadmium were found in and around well-kept homes painted with low-lead paints situated in a small urban community. The implication of such high levels may be quite serious for young children or infants. Children might be expected to have 10 mg of dust on their fingers<sup>11</sup>. If the child spent most of the time indoors and placed the fingers in the mouth ten times, an average of 60  $\mu\text{g}$  of lead and 2  $\mu\text{g}$  cadmium per day would be ingested. If appreciable time were spent outdoors or in a nonresidential setting, these values could be doubled or tripled. Since the maximum permissible daily intake has been estimated at 70 to 500  $\mu\text{g Pb/day}$ <sup>11</sup>, these ingestion values represent significant amounts of lead. The estimated cadmium intake for adult non-smokers is 20 to 50  $\mu\text{g/day}$ , almost totally from food<sup>12</sup>. Children might be expected to take in approximately one-half the adult food level<sup>13</sup>. Therefore, cadmium ingestion from dusts could be a significant fraction of their daily intake.



These levels could represent dangers to children previously thought to be at no risk from paint-induced lead poisoning. A danger from cadmium is also shown to be present in a nonfood source.

### CHARACTERIZATION

The objective of this phase of the project is to characterize the physical and chemical nature and the behavior of particulate material present in the urban environment. Emphasis is placed on material which contains substantial levels of lead, cadmium, and polycyclic organic molecules (POM). Specific questions which are being investigated include:

1. What are the origins and transportation pathways of particles containing lead, cadmium, and POM?
2. What are the physical and chemical characteristics of lead, cadmium, and POM and of the particles which contain them?
3. What are the processes of formation and transformation which determine the nature of particulate lead, cadmium, and POM?
4. How do the physico-chemical characteristics and behavior of particulate lead, cadmium, and POM influence the environmental impact of these pollutants?

The types of particles studied to date are classified into two categories:

1. Environmental particles
  - urban aerosols
  - roadside dusts
2. Source particulates
  - automobile exhaust particles
  - municipal incinerator fly ash
  - fly ash from coal-fired power generation
  - paint flakes

Further environmental particle types (e.g., indoor dusts and soils) will be studied during the next phase of the project, since information on lead and cadmium levels has now been obtained as part of the sampling phase of the Urban Dust project.

Much of the work undertaken during the initial phase of the project has involved method development. This is described, as appropriate, in the sections for which it was required.

### Airborne Particles

The study of airborne particles has progressed in two areas. First, studies were conducted on the attainable precision in determining particle mass and elemental concentrations as a function of aerodynamic particle size using conventional cascade impactors. Natusch and Wallace<sup>14</sup> found that in most aerosol sampling situations mass is greatly overestimated, with errors as great as 100 times in determining the masses of the largest and smallest particles present. For lead, which is bimodally distributed in urban aerosols<sup>15</sup>, the results showed that commonly used cascade impactors gave grossly distorted size distributions. Tests of various surfaces with an Anderson Hi Vol 5-stage cascade impaction head showed that glass fiber surfaces were most suitable for determining mass distributions of urban aerosols.

The second area of study has been an investigation of procedures for quantitative extraction of POM from particles for subsequent determination by fluorometry, gas chromatography, and combined gas chromatography-mass spectrometry. An extraction procedure has been developed with dimethyl sulfoxide (DMSO), and the results will soon be published. Most published values for POM levels in urban aerosols are probably about 30 percent too low as a result of nonquantitative extraction of POM by benzene.

Overall, it is now possible to determine POM levels as low as 1 ng/ml (expressed as pyrene) in DMSO using fluorometry. The combined methodology for quantitative extraction of POM, isolation from aliphatics, and fluorometric determination is therefore considered suitable for determination of POM (as "total fluorescible material") in airborne particulates.

To achieve analyses for individual POM, gas chromatographic and combined GC-mass spectroscopic procedures have been developed.

Identification of individual POM by GC-mass spectrometry has indicated that some 30 compounds provide mass spectra suitable for identification. These spectra are currently being compared with library spectra using computer search facilities. Initial indications are that some 60 to 100 individual POM can be identified in the urban aerosol samples collected.

### Roadside Dusts

In the past year considerable emphasis has been placed on characterization of lead and cadmium in roadside dusts. Results of the sampling phase of urban dust research established that high levels of lead and, to a lesser extent, cadmium are present in dusts collected on and near roadways. The lead almost certainly originates from automobile exhausts.

A bulk sample of roadside dust was sequentially subdivided by physical size, density, and ferromagnetic character and then analyzed. A total of 19 elements were determined in 40 subsamples. The data obtained for lead and cadmium and the mass distribution of the dust are presented in Tables 13-19. Similar data sets are available for the other elements.

Scanning electron microscopic and x-ray spectroscopic analyses of lead-containing particles were performed. It should be stressed that x-ray spectroscopic analysis of individual particles is far from quantitative and that quantitative interpretations of compound stoichiometry based on elemental ratios should therefore be treated with extreme caution. Nevertheless, these results are consistent with the general concept that freshly deposited particulates consist mainly of  $\text{PbBrCl}$ , that preferential loss of Br occurs, and that eventually formation of compounds such as  $\text{PbSO}_4$ ,  $\text{PbCl}_2$ , and PbO (as  $\text{PbO}_2$ ) takes place. These studies provide no evidence about whether such transformations occur in the atmosphere or after deposition. In view of the large aerodynamic diameter of the particles studied, however, we incline to the view that transformation takes place *after* deposition in the roadside dust layer.

Table 13  
Mass Balance for Sieved Fractions

Sub Sample Designation	Size Range ( $\mu\text{m}$ )	Weight (grams)	% of Total Mass
2	250-500	260	40.0
3	100-250	201	30.9
4	75-100	122	18.8
5	45-75	46.5	7.2
6	20-45	18.5	2.8
7	<20	<u>2.0</u>	<u>0.3</u>
		650.0	100.0

Table 14  
Mass Balance of Separated Dust  
(in grams)

Density → Size ↓	<1.6	1.6-2.2	2.2-2.9 (N/M)*	>2.9 (N/M)*
250-500	8.04	2.76	200.21 1.4	40.19 7.4
100-250	5.07	3.32	144.89 1.0	41.73 5.0
75-100	1.69	3.27	61.42 3.3	46.32 6.0
45-75	1.74	0.96	26.80 1.1	14.01 1.9
20-45	0.34	0.90	15.30 0.095	1.76 0.105

\* N = Nonmagnetic fraction (top of diagonal).

M = Magnetic fraction (bottom of diagonal).

Table 15  
 Percentage Mass Balance in  
 Separated Dust  
 (%)

Density → Size ↓	<1.6	1.6-2.2	2.2-2.9 (N/M)*	>2.9 (N/M)*
250-500	1.24	0.42	30.80 0.22	6.18 1.14
100-250	0.78	0.51	22.29 0.15	6.42 0.77
75-100	0.26	0.50	9.45 0.51	7.13 0.92
45-75	0.27	0.15	4.12 0.17	2.16 0.29
20-45	0.05	0.14	2.35 0.01	0.27 0.02

\* N = Nonmagnetic fraction (top of diagonal).

M = Magnetic fraction (bottom of diagonal).



Table 16  
 Concentration of Lead  
 in Separated Dust  
 ( $\mu\text{g/g}$ )

Density $\rightarrow$ Size $\downarrow$	<1.6	1.6-2.2	2.2-2.9 (N/M)*	>2.9 (N/M)*
250-500	2829	2610	321 1696	1398 9155
100-250	4331	2963	513 2177	4214 13,023
75-100	3857	3429	1276 3422	3656 22,131
45-75	4272	5060	1018 2360	4494 19,030
20-45	3839	3557	1327 1649	8957 13,314

\* N = Normagnetic fraction (top of diagonal).

M = Magnetic fraction (bottom of diagonal).

Table 17  
Mass Balance of Lead in  
Separated Dust  
(%)

Density → Size ↓	<1.6	1.6-2.2	2.2-2.9 (N/M)*	>2.9 (N/M)*
250-500	2.31	0.74	6.64 0.24	5.80 7.14
100-250	2.23	1.00	7.56 0.21	17.89 6.73
75-100	0.69	1.17	8.33 0.97	1.80 11.34
45-75	0.74	0.39	2.71 0.26	6.25 3.49
20-45	0.12	0.28	1.77 1.37	0.01 0.13

\* N = Nonmagnetic fraction (top of diagonal).

M = Magnetic fraction (bottom of diagonal).

Table 18  
Concentration of Cadmium in  
Separated Dust  
( $\mu\text{g/g}$ )

Density → Size ↓	<1.6	1.6-2.2	2.2-2.9 (N/M)*	>2.9 (N/M)*
250-500	3.37	3.39	0.35 2.37	0.72 7.44
100-250	5.64	3.70	0.58 5.25	3.01 6.74
75-100	7.71	4.43	1.37 11.80	2.66 10.77
45-75	8.81	7.44	1.42 7.00	3.83 14.12
20-45	6.53	6.21	1.82 5.32	6.81 8.78

\* N = Nonmagnetic fraction (top of diagonal).

M = Magnetic fraction (bottom of diagonal).

Table 19  
 Mass Balance of Cadmium in  
 Separated Dust  
 (%)

Density → Size ↓	<1.6	1.6-2.2	2.2-2.9 (N/M)*	>2.9 (N/M)*
250-500	2.60	0.90	6.84 0.32	2.82 5.47
100-250	2.79	1.20	8.21 0.49	12.28 3.35
75-100	1.32	1.45	8.55 3.99	12.51 6.56
45-75	1.47	0.69	3.63 0.75	5.12 2.49
20-45	0.19	0.46	2.33 1.00	0.04 0.08

\* N = Nonmagnetic fraction (top of diagonal).

M = Magnetic fraction (bottom of diagonal).

Considerable emphasis has been placed on the development of instrumentation capable of determining the actual chemical compounds in which lead and cadmium exist at trace ( $\sim$ ng) levels. This instrumentation is still in the development stage but is expected to be completed within the next 3 to 4 months. Initial studies of lead and cadmium, however, have shown that at least 5 distinct forms of lead are present in composite roadside dust samples. The compounds  $\text{PbSO}_4$ ,  $\text{PbCl}_2$ , and possibly  $\text{PbBrCl}$  have been identified. At least two forms of cadmium exist, one of which is probably  $\text{CdCl}_2$ .

### Paint Particles

Results of scanning electron microscopic studies of paint chips show that leaded paint chips are readily distinguishable from auto exhaust particles containing lead, since they are usually large ( $>30 \mu\text{m}$ ) and contain substantial amounts of lead. These features make it possible to locate them by the technique of elemental mapping in the scanning electron microscope.

Studies have also been conducted to determine whether it is possible to distinguish between leaded paint chips from different sources. The results show that lead chromate road marking paint is readily identifiable by the presence of chromium. However, even samples of essentially similar leaded paints from different manufacturers can be distinguished. Several house paints were studied and it was shown that the  $\text{Pb/Si}$  and  $\text{Pb/Ti}$  ratios (but not the  $\text{Pb/Al}$ ) ratios were statistically sufficiently different to enable distinction. To obtain such distinction it is, however, necessary to observe a sufficiently large paint chip ( $>50 \mu\text{m}$ ) to average over surface irregularities which occur as a result of the granular nature of paint.

These studies are of some importance to the Urban Dust project since they indicate that analytical electron microscopy can be employed to provide information about the origins of lead-containing particles present in samples containing high levels of lead. It should be stressed, however, that subdivision of bulk samples is a necessary adjunct to this technique since it enables selective preconcentration and thus reduces the labor of searching for lead-containing particles.

### Automobile Exhaust Particles

Detailed scanning electron microscopic studies of automobile exhaust particulates have been conducted for the twofold purpose of (1) determining their morphological and chemical characteristics and (2) establishing unique characteristics which can be used for identification purposes.

Particles collected from auto exhausts were shown to be of two types: small spherical particles containing only Pb, Br, and Cl (presumably as PbBrCl) and larger particles containing such elements as Fe, Al, Si, and Ca, apparently with PbBrCl deposited on the surface. These findings strongly support the idea that large ( $>5\text{ }\mu\text{m}$ ) lead-containing particles derived from automobile exhausts enter into the engine with intake air or result from wear within the exhaust system. It is suggested that lead (as PbBrCl) is deposited on the surface of these particles either by fusion of essentially molten PbBrCl droplets or by condensation from the vapor phase or both. In either case this mechanism explains the observation that the mass distribution of lead derived from automobile exhausts is bimodally distributed. Further experiments are being planned to validate this mechanism and to investigate the process of formation of the small spherical particles.

### Municipal Incinerator Fly Ash

Preliminary studies have been conducted to establish the morphological and chemical characteristics of individual fly-ash particles from municipal incinerators. The objectives of this work are to seek identifying characteristics and to investigate the distribution of lead and other trace elements within individual particles using analytical electron microscopy.

Results obtained by Gordon *et al.*<sup>16</sup> show that incinerator fly ash is highly enriched in many trace elements including lead and cadmium. Our studies indicate that it is possible to distinguish such particles from other source particulates containing lead on the basis of their approximately spherical form coupled with the fact that a substantial number of trace elements are usually detectable by x-ray analysis under the electron microscope. There appears to be



considerable variation in the number and type of observable elements between particles, but Pb, Mn, Ni, and Zn were frequently found in our samples.

Analyses of particle interiors and outside surfaces showed that the observed trace elements all predominated on particle exteriors. This finding is in accord with the supposition that many trace elements, including lead and cadmium, are volatilized during combustion and then condense onto the surface of entrained particles as the temperature falls.

#### Fly Ash from Coal Combustion

Extensive studies have been conducted of lead, cadmium, POM, and a large number of trace elements present in fly ash derived from the combustion of coal in power plants. This work is, in part, sponsored by the U. S. Environmental Protection Agency and the results pertinent to the potential combustion of fly ash to urban aerosols and dusts will be summarized here.

Studies of fly ash particles showed that four morphological types exist. Each type is readily identifiable by analytical electron microscopy so that assignment of origin is straightforward. Results of these morphological studies are being prepared for publication.

The aerodynamic size dependences of a number of elements have been determined in several fly ashes and the results published by Davison, Natusch, Wallace, and Evans<sup>17</sup>. These results show that many trace elements, including lead and cadmium, are preferentially concentrated in small, respirable particles. A mechanism of volatilization followed by condensation onto entrained particle surfaces is postulated to explain this phenomenon. Based on this type of mechanism, the potential influence of particle size on inhalation toxicology of trace metals in general, and lead in particular, has been discussed and assessed by Natusch and Wallace<sup>18</sup>.

As in the case of automobile exhaust particulates and incinerator fly ash, a number of volatilizable elements were found to predominate on the surface of coal fly ash. The data show that for particles smaller than about 5  $\mu\text{m}$  essentially

all the lead is present within 100 to 200 Å of the particle surface (Figure 6). For a fly ash whose bulk lead concentration is 900 µg/gm, the actual surface concentration is in fact several percent. Furthermore, initial results show that essentially all of the lead and cadmium can be leached from the surface of fly ash particles by continuous washing with distilled water.

These results will soon be published in *Science* by Linton, Loh, Natusch, Evans, and Williams<sup>19</sup>. The surface predominance of many toxic species is of great importance because it ensures that the highest possible concentrations of many toxic trace elements are in direct contact with environmental and biological extracting fluids and with biological tissues. Furthermore, as is apparent from results reported for particulates from other urban sources, the phenomenon of surface predominance is extremely widespread.

We suggest, therefore, that much greater attention should be given to determination of trace elements, especially lead, on particle surfaces and that bulk analytical data provide a poor insight into the potential toxicity and environmental behavior of many trace elements.

#### Associated Polycyclic Organic Matter (POM)

Extensive studies are being conducted to determine the identity, amounts, and nature of POM associated with coal fly ash particles and to elucidate the way in which POM becomes associated with particles. Experimental results, along with the known behavior of volatilizable trace elements, suggests that POM is present in the vapor phase at all temperatures within the stack system but that rapid adsorption onto the large available surface of fly ash takes place as the effluent cools rapidly at the stack exit. If this is the case, previously determined POM emission factors for coal-fired power plants are probably low by some 100 to 1000 times, since all have been based on analyses of fly ashes collected at high temperatures (at which POM is in the vapor phase). If these values are in error by that amount, then coal-fired power plants must be considered as major contributors of POM to the atmosphere at a level which is at least comparable to and probably greater than that of automobiles<sup>20</sup>. Furthermore, surface deposition ensures that most of the POM is associated with small respirable particles.

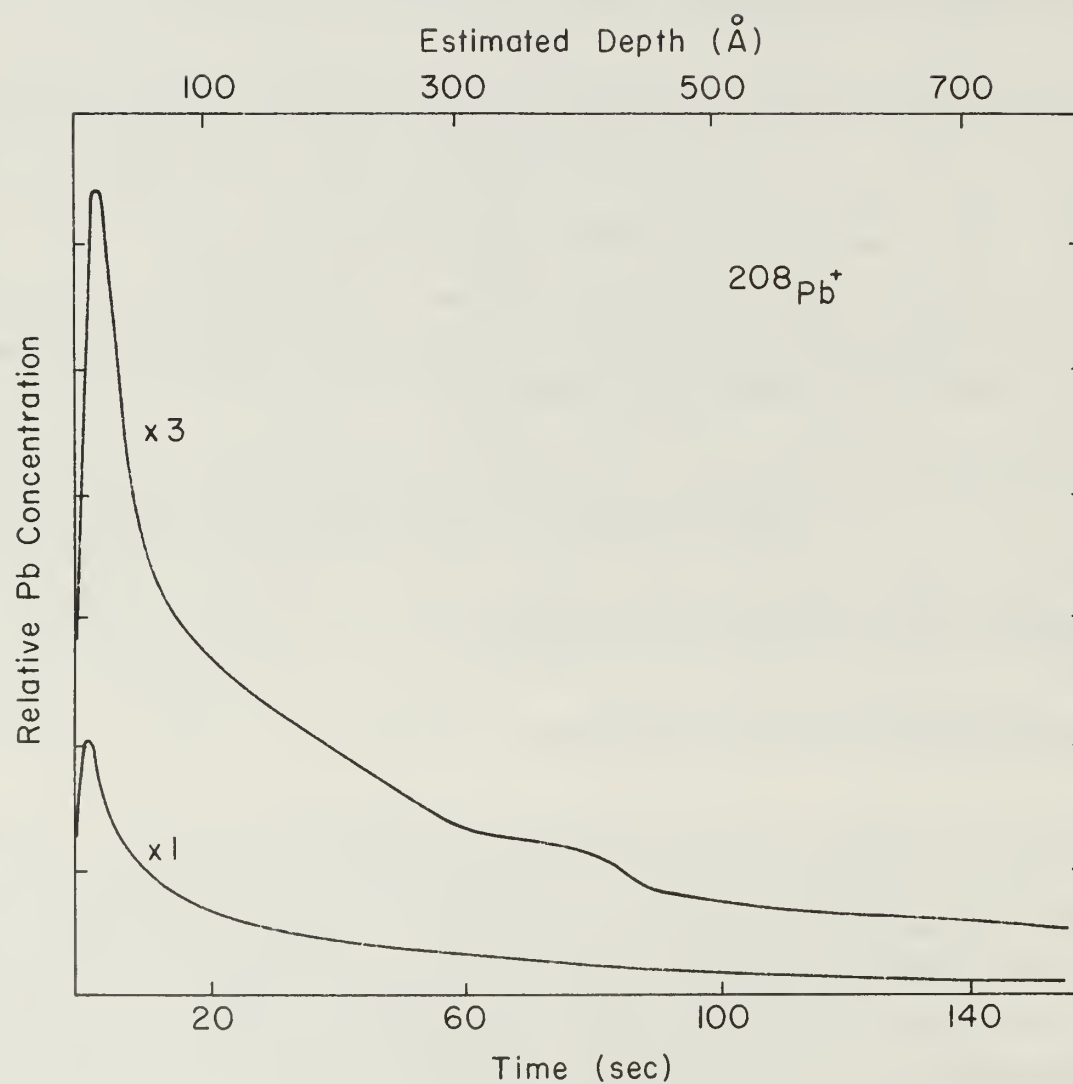


Figure 6. Dependence of lead concentration on depth into a single particle of coal fly ash.

To determine the validity of this adsorption hypothesis, a number of both theoretical and experimental studies were undertaken. Results from a theoretical model showed that if equilibrium conditions are established, the ratio of POM adsorbed to POM in the vapor phase will vary with temperature according to a function of the form presented in Figure 7. (Note that the ordinate represents a *relative* logarithmic scale). Subsequent results of experiments to determine rates of adsorption gave very similar results. It was shown that the net rate of adsorption of POM into fly ash is extremely rapid. In fact, under conditions likely to occur in a power plant stack, equilibrium would be attained within a few seconds.

Experimental validation by both ion microprobe mass spectrometry and Auger microprobe spectroscopy has established beyond doubt that organic material is almost exclusively surface deposited on fly ash collected just outside a power plant stack (Figure 8). These studies indicate that there is a close similarity between the behavior of volatilizable metal species and POM in coal-fired power plants. Thus, both deposit on the surfaces of co-entrained particles as the temperature falls.

While these conclusions have been tentatively reached from studies of POM adsorption onto fly ash, the generality of the principles involved strongly suggests that similar behavior occurs in any high-temperature combustion source irrespective of whether it is a coal- or oil-fired power plant, a municipal incinerator, an automobile, a commercial boiler or a domestic fire.

Since there is considerable statistical evidence relating the levels of POM in certain urban regions to the incidence of lung cancer in those regions, the significance of these findings is considerable.

The identification of POM in fly ash is being pursued using combined gas chromatographic-mass spectroscopic analysis as used for airborne particles. Several POM compounds have been tentatively identified.

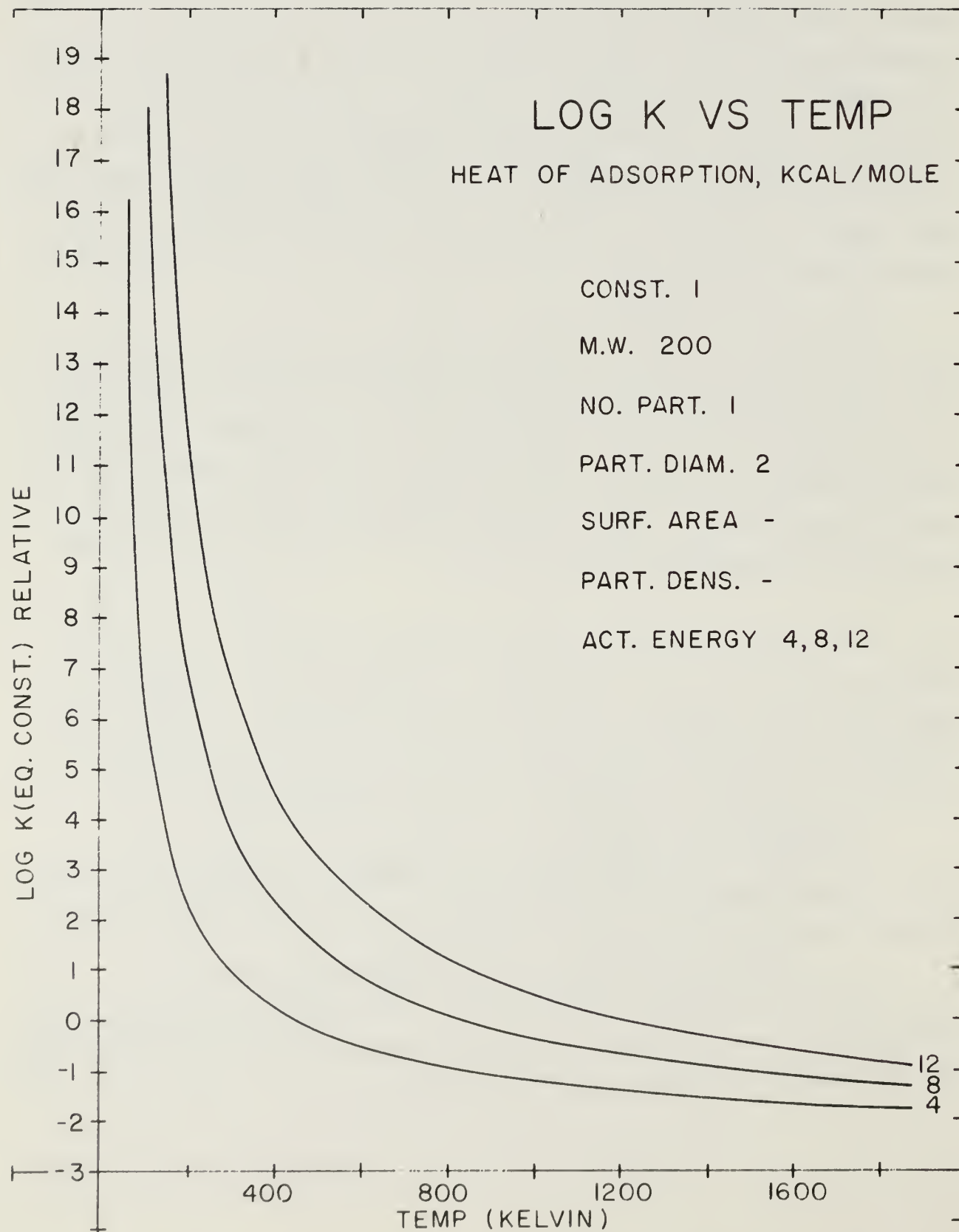


Figure 7. Variation of equilibrium constant, K, with temperature.

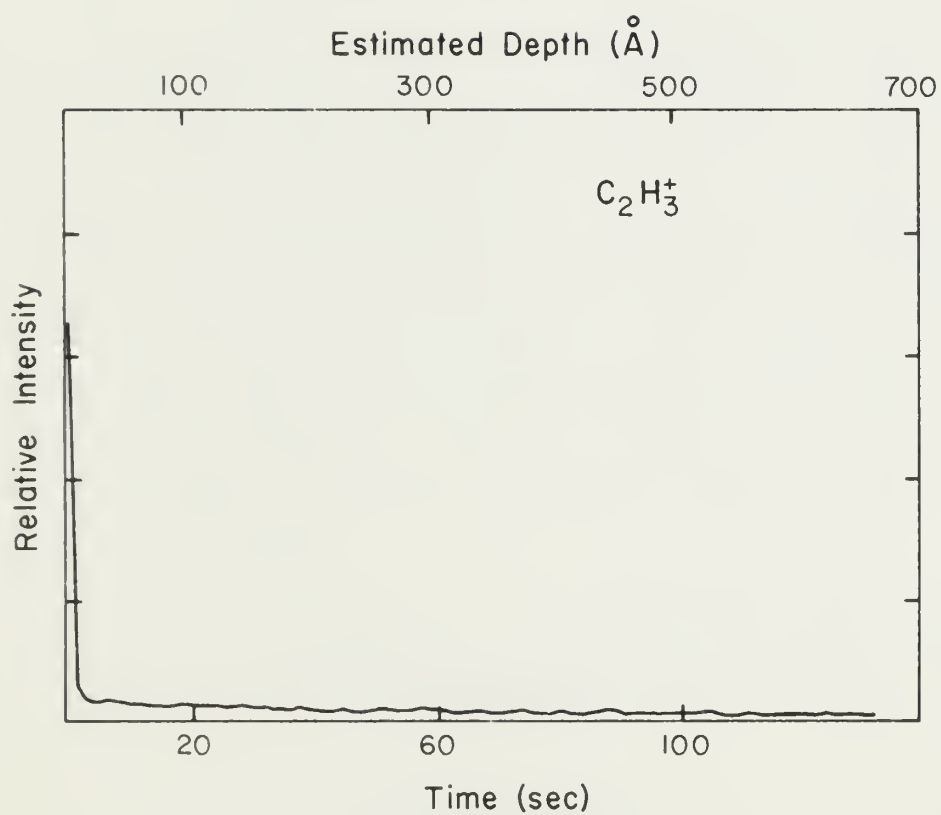


Figure 8. Depth dependence of organic material as represented by the  $C_2H_5^+$  fragment in a single fly ash particle.



While the foregoing studies have indicated that significant amounts of POM are emitted to the atmosphere in association with fly ash from coal combustion, it is important to determine how these molecules are transformed in the atmosphere prior to contacting living organisms. For this reason, studies of the photodecomposition of individual POM associated with airborne particles are being conducted. Initial results from studies of compounds in a nonadsorbing solvent show that photodecomposition occurs quite rapidly, taking place with half times on the order of 5 to 10 minutes under artificial noonday sunlight conditions.

## IV. SYNTHESIS AND MODELING

### MODELING

Different types of models are developed for various purposes. Models may range from general types to be used as research management tools to highly detailed models of specific systems. For this project we are developing a model to be used as a means of synthesizing some of the results of a diversified, interdisciplinary research effort.

One goal of the project is to assess the effects of lead on the growth and yield of crop plant species such as corn and soybeans. Agricultural systems are recognized as being highly complex nonlinear systems. To make estimates of the effects of lead on corn systems we must rely on data that come from a very small subset of the environmental and soil conditions under which crops are grown. In addition, the time span of the experimental data usually covers only a fraction of that required to produce a crop. Because of the complexity of the system, the constraints placed on experimental data, and the need to assess the effects of lead on corn grown in different soils and environments, we believe that a model offers the only feasible method of adequately assessing the effects of lead on corn.

A model is being developed, not to predict corn growth under differing soils and environmental conditions, but rather to predict the effect of lead on corn yield under those varying conditions.

### Model Development

For a model to be useful for our purposes it must have the following properties: (1) it must be possible to extend it beyond the data base from which it is derived and (2) the cost of estimating parameter values for use in other systems must be low in relation to developing a new model. To extend a model to a different system, it is imperative that the model be based on those physical and/or environmental variables known to regulate biological activity.

To maintain adaptability and low cost of conversion to other systems, the driving variables should be easily obtainable. These factors have been considered in developing the Agroecosystem Model (TELOC). The model is driven by local weather data and uses soil characteristics to govern heavy metal uptake.

TELOC is divided into four general sections: (1) meteorological, (2) uptake and water balance, (3) physiological, and (4) growth. Those functions that govern ecosystem behavior (such as rate of photosynthesis or rate of transpiration) are derived from published sources--existing models or papers on individual phenomena. The general structure of the model is derived primarily from deWit, Brouwer, and deVries<sup>21</sup> and secondarily from Curry<sup>22</sup> and from Curry and Chen<sup>23</sup>. The model in its present form is developed to estimate the effects of lead on corn growth and yield.

The meteorological section drives the remainder of the model. Day length, total clear-day solar radiation, and maximum and minimum daily temperatures are data inputs to this section. The model then estimates hourly values of temperature and solar radiation.

Lead movement into the plant is assumed to be a function of the equilibrium concentration of lead (CEQ) in the soil water and the transpirational water flow. The unit of soil considered by the model is 1 gram with a field moisture capacity of 30%. The soil-lead balance is then:

$$\text{Total Lead} = \text{Bound Lead} + \text{Available Lead} \quad (1)$$

Total lead corresponds to soil-sample lead levels at oven-dry conditions. The bound lead is assumed to follow a Langmuir or hyperbolic function<sup>24</sup> and is expressed as a function of CEQ. If equation 1 is rewritten in terms of concentration, the lead balance is:

$$\text{Total Lead} \times (\text{Soil} + \text{H}_2\text{O}) = \text{Bound Lead} \times \text{Soil} + \text{CEQ} \times \text{H}_2\text{O} \quad (2)$$

where

$\text{Soil} + \text{H}_2\text{O}$  = the respective weights of these components in grams.

The bound or sorbed lead is:

$$\text{Bound Lead} = \frac{K_1 \text{ Maxlead} \times \text{CEQ}}{1 + K_1 \text{ CEQ}} \quad (3)$$

where

Maxlead = the maximum sorptive capacity of lead by the soil (a function of cation exchange capacity, pH, and available phosphorus<sup>25</sup>). To solve for CEQ, equation 3 is substituted into equation 2. As we have shown earlier (Modeling Memo #1), CEQ can be treated as a constant with respect to soil moisture content at soil lead levels below about 50% of Maxlead. The movement of lead into the plant is then:

$$Pb_p = TF \times K_2 \times CEQ \quad (4)$$

where

$Pb_p$  = the lead in the plant,

TF = the transpirational water flow,

$K_2$  = a constant,

CEQ = the concentration equilibrium of lead in the soil-water solution.

To test this function, we assumed that TF is proportional to leaf weight and that  $K_2 = 1$ . A logistic growth curve was estimated for leaf weight<sup>26</sup>. A priori estimates of leaf lead concentrations for a greenhouse experiment were made. These values as well as observed values are presented in Table 20. The estimated values differ from the observed values by about 20% at the higher levels. Considering the assumptions involved, the data demonstrate the validity of the approach and the fact that lead uptake is a nonlinear function of soil loading.

Table 20  
Predicted and Actual Concentrations of Lead in Corn Grown in  
Bloomfield Sand

Soil Lead (ppm above background)	Estimated Lead Level (ppm)	Observed Lead Level (ppm)
0	5	6
75	81	85
150	158	220
225	244	295

Additional work with equation 4 indicated a local maximum followed by a local minimum for tissue concentrations. These points are related to organ growth rates and lead uptake rates. This behavior was later confirmed in three experiments.

TELOC uses a modification of functions given by Feddes, Bresler and Neuman<sup>27</sup>. These functions were modified such that transpirational flow goes to zero as plant biomass goes to zero. Figure 9 shows the results of a simulation run of lead uptake by corn grown in Bloomfield soil with 250 ppm lead. Well-defined local maxima and minima are not shown, although there are two inflections in the curve at about 30 and 45 days. The difference between the simulation and lead uptake behavior mentioned earlier may result from problems with the transpiration function or from differing growth patterns. The simulated concentrations are comparable to greenhouse experiments for the time period up to at least day 100.

Hourly rates of photosynthesis and respiration are calculated by the physiology section of TELOC. To estimate photosynthesis, the canopy is divided into 0.1 Leaf Area Index (LAI). Light transmission in the canopy is assumed to follow Beer's law, and the reflection coefficient is 0.2<sup>28</sup>. The light available for photosynthesis at a given level in the canopy is:

$$I_n = 0.8 I_0 e^{-K_3 L(n-1)} \quad (5)$$

where

$I_n$  = the light at the  $n^{\text{th}}$  level,

$I_0$  = the incident short wave radiation,

$K_3$  = the coefficient of transmission (estimated to be 0.054 from Idso and de Wit<sup>29</sup>),

$L_{(n-1)}$  = the number of layers above  $n$ .

The rate of photosynthesis at the  $n^{\text{th}}$  level is then:

$$\text{Phsyn}_n = \frac{K_4 I_n}{K_5 + I_n} \times F_1 \times F_2 \times F_3 \quad (6)$$

where

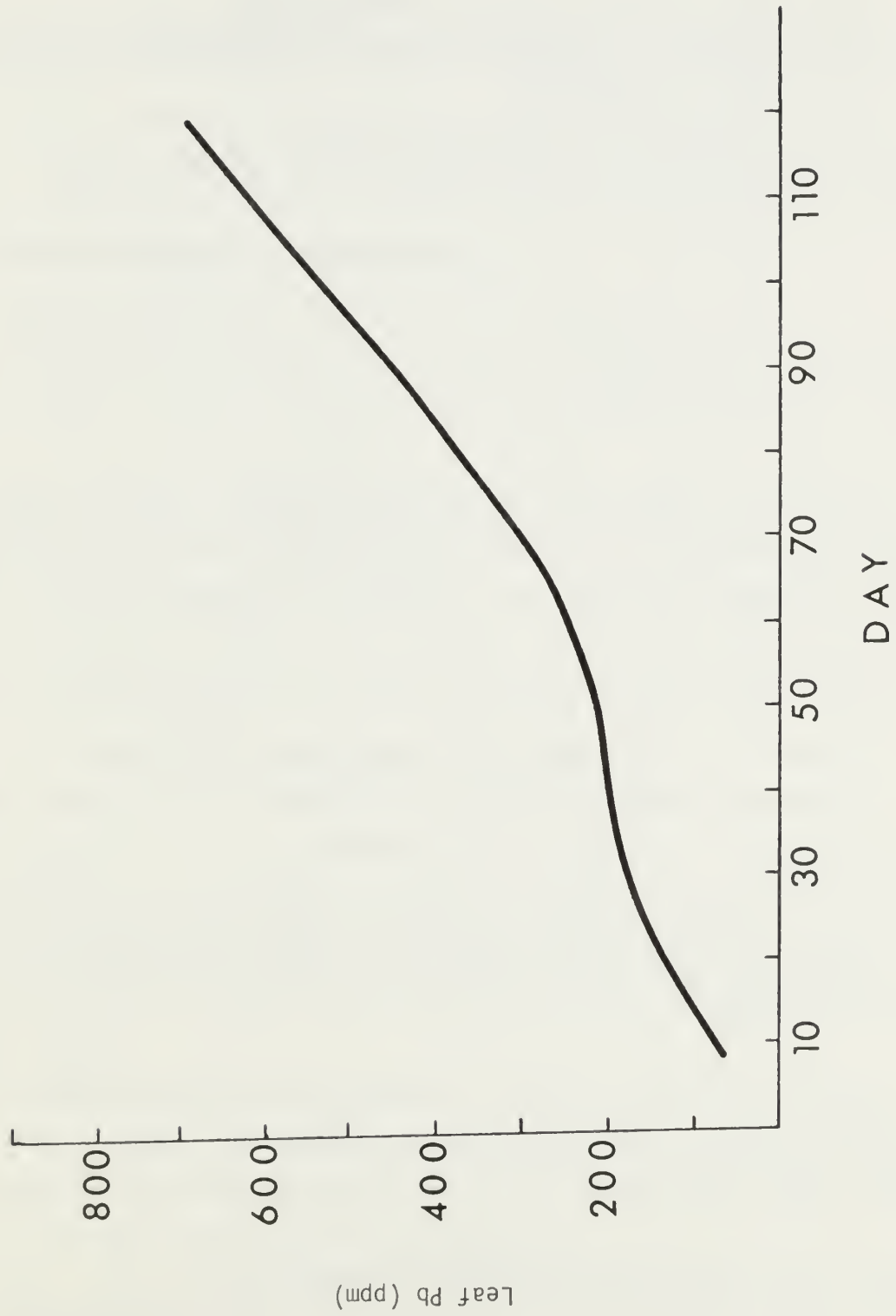


Figure 9. Simulation of uptake of lead by corn grown in Bloomfield soil amended with 250 ppm lead.



$\text{Phsyn}_n$  = the hourly rate of photosynthesis of the  $n^{\text{th}}$  canopy level in  $\text{kg ha}^{-1}\text{day}^{-1}$  (the hyperbolic part of the function comes from de Wit, *et al.*<sup>30</sup>),

$K_4$  = the "saturation rate" of photosynthesis,

$K_5$  = a constant (estimated from Moss and Musgrave<sup>31</sup> as 6.0 and 0.92, respectively),

$F_1$  = a temperature function (from de Wit, *et al.*<sup>32</sup>),

$F_2$  = the effect on photosynthesis of the age of the leaf (assumed to be 1),

$F_3$  = the effect of lead on photosynthesis (estimated to be -5% for each 100 ppm of lead in the leaf from Bazzaz, Rolfe, and Windle<sup>33</sup>).

The total hourly photosynthesis is estimated by summing over canopy levels.

The model estimates a midday rate of photosynthesis of  $30 \text{ kg ha}^{-1}\text{hr}^{-1}$  for a LAI of 1.3 at a light intensity of 0.95 Langleys. The daily rate for these conditions is about  $370 \text{ kg ha}^{-1}\text{day}^{-1}$ . This value is comparable to daily estimates by ELCROS<sup>34</sup> of  $272 \text{ kg ha}^{-1}$  for a LAI of 1.3 but at a lower light intensity.

Respiration is divided into two components, growth respiration and maintenance respiration. The growth respiration rate is assumed to be 1.5; that is, 1.5 kilograms of carbohydrates are used to produce one kilogram of dry matter. Maintenance respiration rate is a function of dry matter and temperature. The function of de Wit, *et al.*<sup>35</sup> is used.

The photosynthate produced is used in two ways: first, to satisfy maintenance respirational needs and, secondly, for growth. Any excess is allocated to generalized stores.

Growth of the various organs is computed by the following type of function, with the growth of leaves given as an example.

$$\text{DWL} = \text{RGRL} * \text{WL} * \text{CNTG} \quad (7)$$

where

DWL = the rate of growth of leaves in  $\text{kg ha}^{-1}\text{hr}^{-1}$ ,

RGRL = the relative rate of leaf growth calculated from Chandler<sup>36</sup>,

WL = the weight of leaves in  $\text{kg ha}^{-1}$ ,

CNTG= the constraints to growth.

CNTG is the link between leaf lead levels and growth. We assume, following de Wit, *et al.*<sup>37</sup>, that CNTG has a value of 1 if stores are greater than 4% of total weight and that they decrease linearly to zero as the percent of stores decreases to zero. Thus, if lead causes sufficient reduction in the photosynthetic rate to cause stores to decrease below 4% of total weight, then the organ growth rate decreases proportionately.

Figures 10 and 11 show simulations of vegetative and reproductive growth for corn grown in Bloomfield sand which contains 250 ppm lead. Leaf levels of lead are shown in Figure 9. A density of 30,000 plants per hectare is assumed.

Figure 10 shows a decrease of about 8% in vegetative growth while yield is decreased by 23%. The large difference between the reduction in grain and that in vegetative growth is caused by the depletion of stores by the rapidly growing vegetative organs. The difference in grain yield amounts to about  $1900 \text{ kg ha}^{-1}$  ( $34 \text{ bu acre}^{-1}$ ) in a total of  $8000 \text{ kg ha}^{-1}$  ( $145 \text{ bu acre}^{-1}$ ).

#### Model Verification and Extension

The model is now in the final stage of formulation. To date, it has been verified only qualitatively; its general behavior compares closely to existing experimental information. We are not yet certain of the model's accuracy and will not be able to verify it quantitatively until next fall after data are available from a planned summer field experiment on corn and soybean yield.

The transpiration section of the model needs a considerable amount of work. Once that section is satisfactorily completed, we will be able to evaluate a potential secondary effect of lead on photosynthesis--its interference with transpiration. We are now investigating alternative functions for estimating evapo-transpiration.

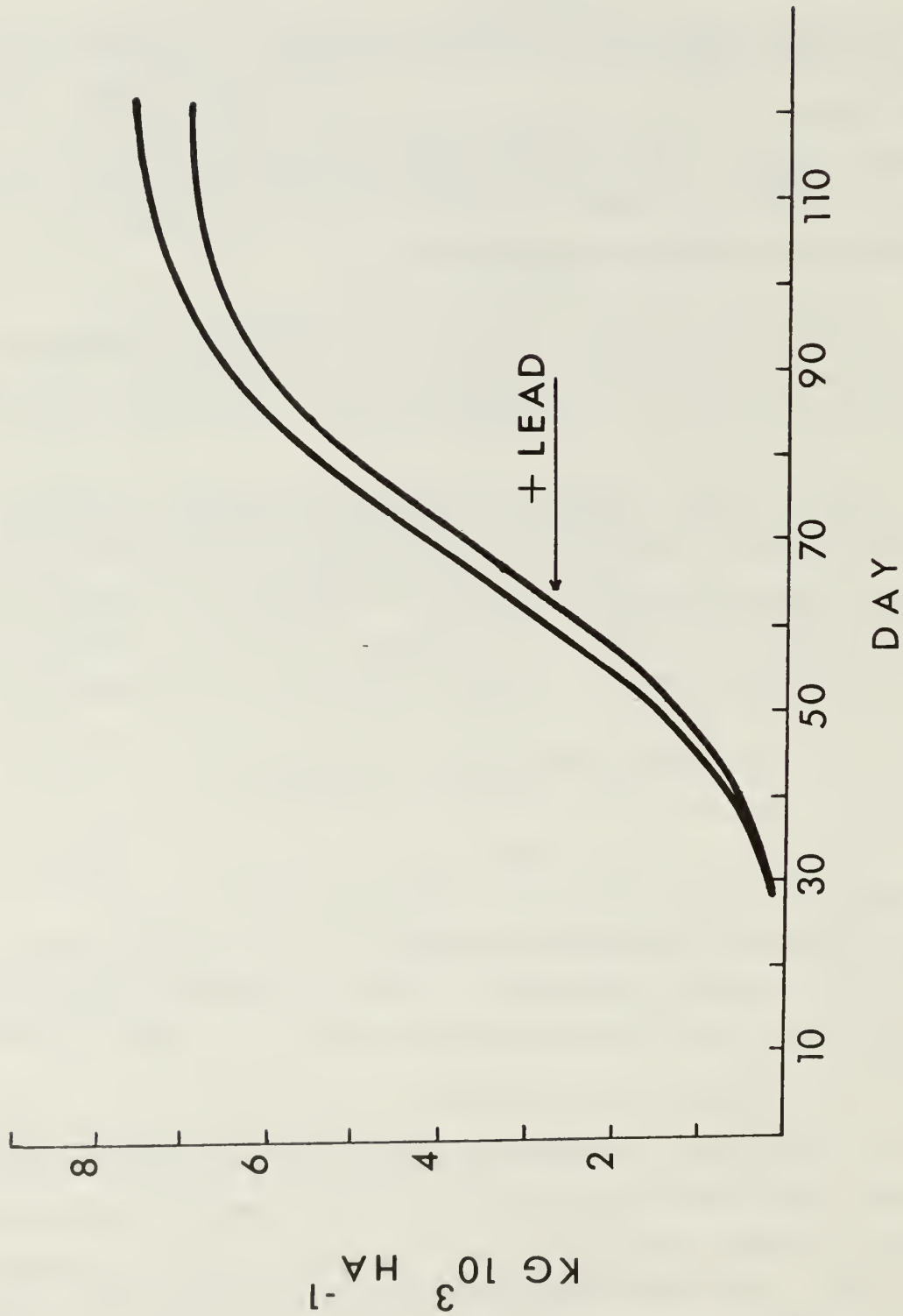


Figure 10. Simulations of vegetative growth for corn grown in non-amended Bloomfield soil and in Bloomfield soil amended with 250 ppm lead.

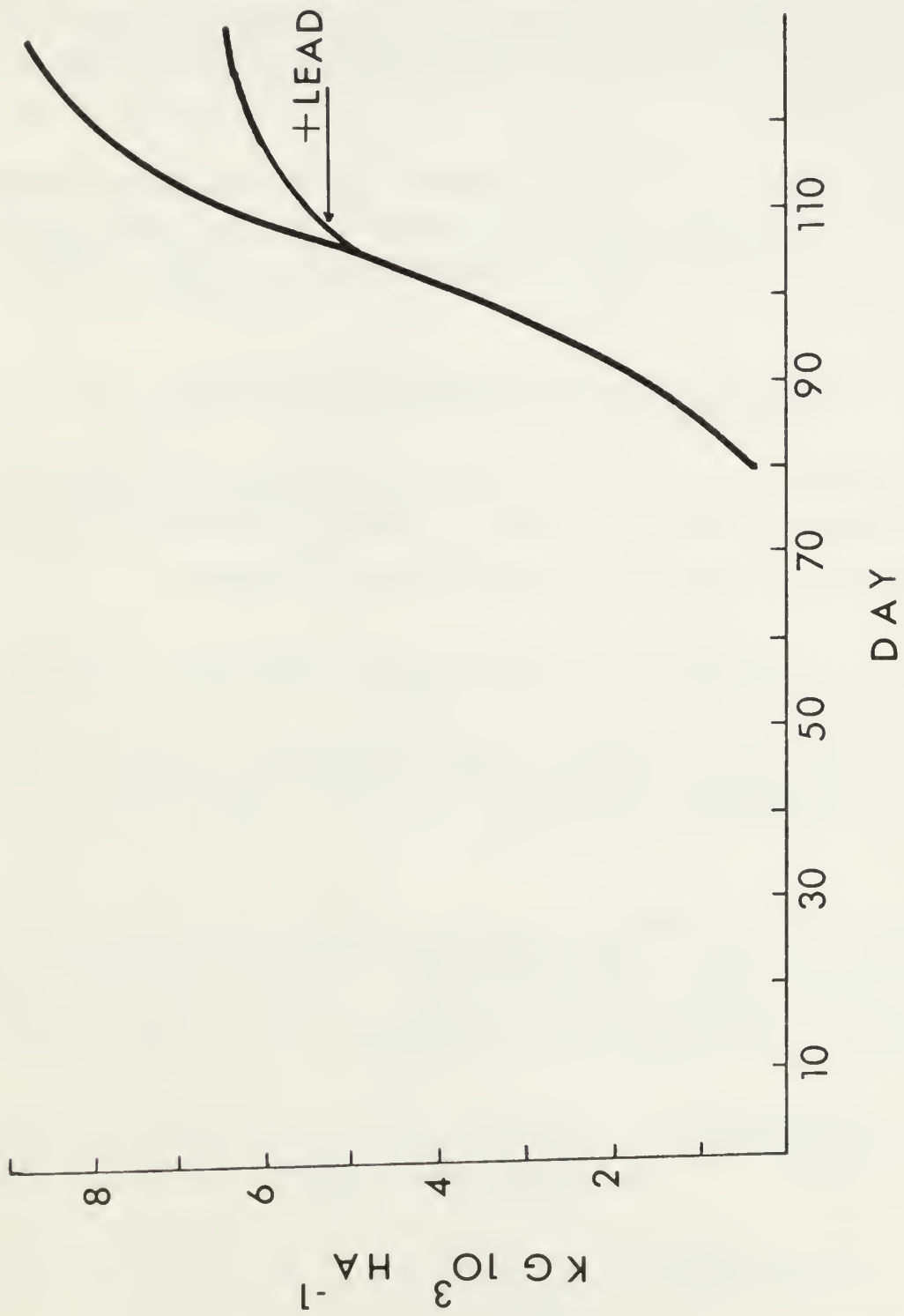


Figure 11. Simulations of grain yield for corn grown in non-amended Bloomfield soil and in Bloomfield soil amended with 250 ppm lead.

With minor changes the model can be used to evaluate the effects of cadmium on corn growth. The final modification proposed for the model is to adapt it for assessing the effects of lead and cadmium on soybean yield. To do so would entail developing new growth and photosynthetic functions.

### RISK/BENEFIT ANALYSIS

Research objectives and accomplishments for this component of the project fall into two categories: analysis of the benefits of using lead in gasoline and analysis of risks from the effects of automotive lead emissions on crops and on human health.

#### Benefit Analysis of the Use of Lead in Gasoline

The objective of the benefit analysis is to develop and estimate an econometric model for forecasting gasoline consumption under different alternatives for controlling the use of lead additives in gasoline.

Nearly all of the required data have been assembled for estimating a simultaneous equation model of gasoline consumption; approximately 80,000 cards have been punched. Data on gasoline consumption, gasoline prices, personal income, new car purchases, and cars in operation have been processed into the appropriate form for econometric analysis.

Because gasoline consumption displays considerable regional variation, the econometric models and corresponding data base have been defined in terms of mixed cross-sectional, time-series variables. The error-components estimation technique is used to estimate the parameters of this kind of model.

Review and synthesis of the properties of error-components estimators have been completed<sup>38</sup>. For the two-component estimator, the minimum variance estimator of the  $r$ -class of estimators was developed. Alternative variance estimators were considered and their relative merit determined. The computer programming needed for the error-components technique has also been developed<sup>39</sup>.

As part of the process of "tooling up" to estimate the simultaneous equation model, we have applied econometric methods to single equation models of gasoline consumption. The results of this research have provided the major

source of material for two invited papers<sup>40, 41</sup>.

Estimates of demand equations were made for both regular and premium grades of gasoline. These estimates are as follows with the standard errors of estimate in parentheses.

For regular gasoline consumption:

$$\ln(q_{it}) = .094 \ln(y_{it}) - .038 \ln(p_{it}) + .847 \ln(q_{i,t-1})$$

(.018)                      (.013)                      (.013)

Where

$q_{it}$  = per capita gasoline consumption in the  $i^{\text{th}}$  state and  $t^{\text{th}}$  time period;

$y_{it}$  = per capita disposable income,

$p_{it}$  = the price of gasoline.

For premium gasoline consumption:

$$\ln(q_{it}) = .421 \ln(y_{it}) - .013 \ln(p_{it}) + .711 \ln(q_{i,t-1})$$

(.077)                      (.012)                      (.039)

The equation for regular gasoline was estimated using data for 49 states and 40 quarters from 1963:1 to 1972:4. The equation for premium was estimated for 15 states and 27 quarters from 1964:4 to 1971:2.

These results are most useful in considering the effects of an increase in gasoline taxes on consumption. If the percentage change in the price of both grades is the same, then the implied short-run price elasticity for gasoline is  $-.032$  while the long run value is  $-.197$ . (These results depend on the fact that 25 percent of current total gasoline sales are of premium grade.) Similar values for income elasticity indicates that a 20-percent price rise will decrease consumption in the long run by 3.9 percent.

#### Risk Analysis of Crop Exposure and Human Health Implications of Automotive Lead Emissions

The objective of this phase of the study is to assess the economic risks to crops and to human health from exposure to automotive lead.



A preliminary analysis of the dollar value of crop damages due to lead emissions was made for Champaign County. Because an exposure-effect relationship between ambient concentrations of lead and crop effects is still under development, various hypothetical levels of crop damages were used in this work.

The method used in this analysis differs somewhat from survey methods that have been used to assess crop damages. The steps are as follows:

- a. Identify and measure the amount of cropland in high-lead-exposure areas.
- b. Subdivide the total area into acreage by crop type.
- c. Determine baseline crop yields by soil type.
- d. Predict crop loss (based on exposure-effect relationships) by soil type and concentration.
- e. Estimate dollar loss.

A preliminary analysis comparing the dollar value of agricultural and human health damages was also made for the State of Illinois<sup>42</sup>. Again in the absence of exposure-effect relationships between ambient lead concentrations, crop effects, and human health effects, various hypothetical values were used in estimating the dollar value for crop and human health damages.

This analysis computed, on one side, the costs of removing lead from gasoline (or the benefits of the continued use of lead). This process requires technological analysis of changes in costs given that the lead is removed and of the ultimate effects of these changes on the supply schedule for gasoline. Second, it requires estimating the gasoline demand schedule. The lowest cost of removing lead from gasoline for Illinois under various assumptions is \$112.8 million annually.

The risks from automotive lead emissions arise in three specific ways considered here. The first is reduction of agricultural yield. The second is the health hazard of lead contamination of agricultural products. Finally, the human health risks of urban air and dust contaminated by lead are considered.

The total loss computed is very preliminary and speculative. For Illinois, the estimated loss is \$23 million annually. The benefits of lead in gasoline are seen to greatly exceed the dollar value of risks, but future research is encouraged to make benefits and risks more specific.

## V. ANALYTICAL LABORATORY

### ROUTINE ACTIVITIES

Because of limitations of funding and the static requests for analysis from the principal Metals Task Force users--the Plant Response and Urban Dust groups--the laboratory effort has been primarily devoted to routine assays as opposed to special analyses and/or development.

During the period October 1, 1974, to October 1, 1975, the laboratory processed a total of 9136 samples and 13,087 assays for this project. Principal sample types have been soils (23%) and plant tissues (36%) from the Plant Response Group and street dust (9%), house dust (7%) and air filters (3%) from the Urban Dust Group. Lead and cadmium were by far the elements for which assays were most frequently requested, but other elements were occasionally requested as well. The major elements assayed, by frequency of request, were Pb (100%), Cd (72%), Fe (5%), Zn (10%), Ni (5%) and Cu (<5%). Atomic absorption remains the dominant form of analysis for this project. Stripping analysis, the only other analytical method applied on a routine basis to this project, was used less frequently than in past years as the sampling of the quondam Total Ecosystem Group completed its stream water analyses.

### METHODS DEVELOPMENT

Because of the longevity of most phases of this project, the laboratory has been able to draw on in-place, tested procedures for the samples submitted during the past year with one exception: street dirt samples from the Urban Dust Group. The combination of extreme sample heterogeneity, the need for both lead and cadmium assays, and an unpredicted sample submission rate required in excess of 300 man-hours of methods development to produce a procedure which gave satisfactory results with a reasonable amount of technician time per sample.

Street-dirt samples were collected by totally vacuuming a selected area with a commercial-duty vacuum cleaner equipped with a clean plastic trash-bag liner. The resulting sample was extremely heterogeneous with particle sizes

ranging from dust to twigs and bottle caps. The presence of the large pieces introduced a subjective character to the subsequent sample treatment since it was not possible to devise an objective method of partitioning the larger pieces of debris by riffing or other sectioning techniques. By agreement with the sample submitter, these samples have been subsequently treated by an initial sieving through a 40-mesh screen to eliminate the larger materials (and also an unknown amount of original sample weight and assayed-for metal). Some early sieving-analysis experiments showed that the larger materials contributed significantly only to the sample weight and not to the total lead-cadmium analyses. Sample heterogeneity of the initial sieved materials was improved but not eliminated for larger samples (greater than 20 grams) which could be subjected to classical size reduction techniques such as quartering and riffing.

A series of experiments on riffled samples in which a larger sample was partitioned into  $2n$  subsamples in  $n$  riffle passes showed that lead assays were statistically identical in the subset but that cadmium results scattered widely. For lack of time, this phenomenon was not pursued but rather sidestepped by analyzing the total submitted sample if it weighed less than 5 grams. Because cadmium assays were routinely requested for these samples, the subsequent treatment was wet ashing with nitric-perchloric acids followed by a return to the more established, routine path to ultimate AA analysis. Because a variety of the problems encountered were compromised rather than solved, the data obtained from street-dirt samples remains the most suspect this laboratory has ever produced.

The second major area of development was in further refinements of data processing techniques. Data handling by computer assistance has been an evolutionary process in this laboratory since its inception. Initially, the laboratory used a user-oriented language and code written in Fortran for the Burroughs 5500 (later the 6700) computer. As a result of rather rapid changes in laboratory operating conditions at the time, the programmers could not keep pace with internal developments. Consequently, this program was obsolete when finished and was never seriously used.

A second-generation code using the same computer was developed in-house by Mr. Robert Zeilinski during the intermediate years (1972-73). It was the initial exercise in incorporating statistical concepts such as minimum data acquisition, signal-to-noise estimates, detection limits, and sensitivities, all applied to the routine analysis of metals by atomic absorption. In this program a measurement was based on a fixed set of four digital data points obtained from the DVM readout of the JACO 810 AA unit--two base line points and two top-of-curve points.

A combination of difficulties associated with using the Burroughs machine induced the laboratory to transfer operations to the Center for Advanced Computation PDP 11/50 system to use its "excess" processing time. This machine uses a language, "C", specifically tailored to take advantage of the computer architecture. This change required major rewriting of the existing Burroughs 6700-based DATAFLOW program. In the process a number of improvements have been made. Data is now acquirable in user-defined units of  $2^n$  numbers per measurement rather than the inflexible 4 per measurement of DATAFLOW. In addition, the new program computes an individual error estimate based on the base-line noise estimate immediately preceding the top-of-the-curve data. A running accumulated batch estimate is simultaneously acquired. Detection limits are expressed uniquely for each sample. As in the original program, the newer code calculates the slope of a linear curve for the element as a running operation based on each insertion of a labeled standard and increments or decrements the sensitivity as required in a linear interpolation fashion between the last previous standard estimate and the updated value. Improvements in formatting of the data output also have been instituted in this process. Running records of laboratory assays are recorded and updated weekly with a printout which serves as a distribution copy to interested personnel. Backup files of all analyses reported are now in operation as spin-offs. It is expected that the amount of technician and management time spent in data handling will be substantially reduced by these changes.

Other developments worthy of note are: (1) a rapid method for estimation of high (few ppm) levels of zinc, cadmium, lead, and copper in soil samples based on cold acid digestion, buffered solution neutralization, and final



estimation by Pulse Polarography (developed primarily for another project), (2) a flameless AA method for total ambient mercury in air based on gold amalgam collection (developed under a contract with the Illinois Environmental Protection Agency with support from the Illinois Institute for Environmental Quality), and (3) emission spectroscopic determination of metals in soil cores (referee method for x-ray fluorescence spectroscopic determinations).

#### FUTURE WORK

Estimates of sample load for the next year, as modified by budgetary realities, indicate a probable load in the range from 8000 to 9000 samples. Sample types, as listed by the user groups, are not substantially different from the past with the exception of urban dust samples to be assayed for multiple elements.

Staffing for this year has been reduced and changed in composition as part of an ongoing process of evolution to a laboratory operation having flexibility for responding to the needs of future projects. A recently completed time study indicated the desirability of shifting to a predominantly low-skills laboratory helper staff monitored by a minimum of skilled analytical chemical technicians. In part, this change is induced by recent and predicted future shifts to a "raw sample" mode, requiring more sample pre-preparation by laboratory personnel. The necessary sample preparation steps are best handled by the less expensive low-skills personnel. In equal measure, this change represents a deliberate shift from a labor-intensive to a capital-intensive operation which will be made possible by the temporary nature of student help.

The laboratory has now operated for over four years largely on the techniques and methods developed during its first 5 months of existence. Methods inserted in the interim have been limited to those most necessary and have been investigated only to the extent needed to establish them with reliability. As a result, the laboratory does not have a spectrum of readily accessible methods to assist members of this project who might desire the occasional opportunistic assay of an unusual element. Steps are being taken to remedy this



condition by releasing some of the assistant laboratory director's time to add selected published methods to the laboratory's established routines. Among the target methods are (1) general emission spectrographic procedures as backup and/or referee methods to support XRF and INAA measurements, (2) Massman furnace flameless AA methods for frequently requested elements, and (3) kinetic methods of analysis.

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<sup>41</sup>Provenzano, G., and R. Resek. 1975. The demand for gasoline: a statistical analysis of policies for altering total consumption. Paper presented at the Joint Statistical Meetings of the American Statistical Association, August 25-28, 1975, at Atlanta, Georgia.

<sup>42</sup>Resek, R., and G. Provenzano. 1975. The risks and benefits from lead in gasoline: effects on energy use and environment. Paper presented at the International Conference on Regional Science, Energy and Environment, Center for Economic Studies, May 22-25, 1975, at Catholic University, Louvain, Belgium.



## APPENDIX: PROJECT-RELATED SEMINARS, PRESENTATIONS, AND PUBLICATIONS

### PROJECT SEMINARS

March 6, 1975                      Research review of the project.

May 6, 1975                      Informational seminar for persons (primarily agriculturalists) interested in heavy metals and plant effects. Conclusions of the ecosystem study as well as results of the plant response and urban dust studies were discussed.

#### Plant Response Group Seminars

In a series of seminars the Plant Response Group members listed below presented the results of their studies to other members of the project:

October 2, 1975                  G. L. Wheeler

October 9, 1975                  J. J. Hassett and J. E. Miller

October 16, 1975                F. J. Stevenson and M. Cole

November 6, 1975               R. W. Carlson, J. J. Stukel, and D. Lane

### PAPERS AND OTHER PRESENTATIONS

May 1974                      "Physico-Chemical Factors Influencing Urban Aerosol Toxicity."  
Seminar presented by D. F. S. Natusch to the Department of Physiology in the Medical School at Yale University in New Haven, Connecticut.

May 1974                      "Physico-Chemical Factors Influencing Urban Aerosol Toxicity."  
Seminar presented by D. F. S. Natusch at the School of Public Health at the University of Michigan in Ann Arbor.

May 1974                      "Physico-Chemical Factors Influencing Urban Aerosol Toxicity."  
Seminar presented by D. F. S. Natusch at the Lawrence Berkeley Laboratory, Berkeley, California.

June 1974                      D. F. S. Natusch, "Preferential Concentration of Toxic Species on Small Airborne Particles."  
Presented by the author at the Air Pollution Control Conference in Denver, Colorado.

September 1974                "Analytical Needs in Environmental Protection."  
Seminar presented by D. F. S. Natusch at the Bound Brook Research Laboratories, American Cyanamid Company.



- September 1974 J. E. Miller, J. J. Hassett, D. E. Koeppe, G. L. Rolfe, and G. L. Wheeler, "Effects of Soil Properties on Pb Uptake by Corn and Effects of Pb and Cd on Corn Root Elongation."  
Presented by G. L. Wheeler at the Second Annual NSF Trace Contaminants Conference in Asilomar, California.
- October 1974 R. S. Vogel and A. M. Hartley, "Signal Characterization and Measurement in Microsample Atomic Absorption Spectroscopy."  
Presented by R. S. Vogel at the Seventh Annual Research Symposium: Accuracy in Trace Analysis conducted by the National Bureau of Standards in Gaithersburg, Maryland.
- December 1974 J. J. Stukel, R. L. Solomon, and J. L. Hudson, "Atmospheric Transport of Lead from Automobile Exhaust."  
Presented by R. L. Solomon at the 16th Annual Meeting of the American Institute of Chemical Engineers in Washington, D. C.
- December 1974 D. F. S. Natusch taped a 15-minute radio presentation on his work in the Urban Dust Group. Released by the American Chemical Society simultaneously with a press release.
- January 1975 G. L. Rolfe, "Lead Transport and Distribution in a Watershed Ecosystem"  
Presented by author at the Annual Meeting of the American Association for the Advancement of Science in New York, N.Y.
- January 1975 "Physico-Chemical Characterization of Trace Contaminant Association in Airborne Particles."  
Seminar presented by D. F. S. Natusch to the Department of Chemistry at Colorado State University in Fort Collins.
- March 1975 R. Lamb and D. F. S. Natusch, "Determination of Thallium in Environmental Particulates."  
Presented by R. Lamb at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in Cleveland, Ohio.
- March 1975 A. Loh and D. F. S. Natusch, "Microscopic Characterization of Coal Fly Ash Particulates."  
Presented by A. Loh at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in Cleveland, Ohio.
- March 1975 "What Little We Know about Global Air Pollution."  
Seminar presented by D. F. S. Natusch to the Local Section of the American Chemical Society, Springfield-Decatur, Illinois.
- March 1975 D. F. S. Natusch, "Characterization of Atmospheric Pollutants from Power Plants."  
Presented by the author at the 2nd ICMSE Conference on the Great Lakes, Argonne National Laboratory in Argonne, Illinois.

- April 1975 D. F. S. Natusch, "Physico-Chemical Associations of Trace Contaminants in Coal Fly Ash."  
Presented by the author at the Meeting of the American Chemical Society in Philadelphia, Pennsylvania.
- April 1975 "Environmental Impact of Trace Metals."  
Seminar presented by D. F. S. Natusch at the University of Missouri in Columbia.
- April 1975 "Lead Transport and Distribution in a Watershed Ecosystem."  
Seminar presented by K. A. Reinbold to the Botany Department at the University of Illinois at Urbana-Champaign.
- April 1975 F. J. Stevenson, "Binding of Metal Ions by Humic Acids."  
Invited paper presented by author at the Second International Symposium on Environmental Biogeochemistry in Burlington, Ontario.
- May 1975 J. B. Wedding, R. W. Carlson, J. J. Stukel, and F. A. Bazzaz, "Aerosol Deposition on Plant Leaves."  
Presented by R. W. Carlson at the First International Symposium on Acid Precipitation and the Forest Ecosystem at Ohio State University in Columbus.
- May 1975 R. Resek, "The Risks and Benefits from Lead in Gasoline: Effects on Energy Use and Environment."  
Presented by author at the International Conference on Regional Science, Energy, and Environment conducted by the Center for Economic Studies at Catholic University in Louvain, Belgium.
- May 1975 "Physical and Chemical Factors Influencing the Toxicity of Urban Aerosols."  
Seminar presented by D. F. S. Natusch at the Center for Air Environment Studies at Pennsylvania State University in State College, Pennsylvania
- June 1975 G. Provenzano, "A Comparative Analysis of Alternative Economic Policies for Reducing Gasoline Demand."  
Presented by author at the Western Economic Association 50th Annual Conference in San Diego, California.
- August 1975 R. Resek, "Revised Error Components: More Efficient Estimation with Combined Cross Section and Time Series."  
Presented by author at the World Congress of the Econometric Society in Toronto, Ontario.
- August 1975 G. Provenzano and R. Resek, "The Demand for Gasoline: A Statistical Analysis of Policies for Altering Total Consumption."  
Presented by authors at the Joint Statistical Meetings of the American Statistical Association in Atlanta, Georgia.

- August 1975 G. L. Rolfe and K. A. Reinbold, "An Interdisciplinary Study of Environmental Pollution by Lead and Other Metals."  
Presented by K. A. Reinbold at the 26th Annual Meeting of the American Institute of Biological Sciences at Oregon State University in Corvallis.
- August 1975 R. W. Carlson, F. A. Bazzaz, and J. J. Stukel, "Physiological Effects, Wind Reentrainment, and Rainwash of Lead Aerosol Particulate Deposited on Plant Leaves."  
Presented by R. W. Carlson at the 26th Annual Meeting of the American Institute of Biological Sciences at Oregon State University in Corvallis.
- August 1975 A. Loh, J. E. Baker, C. A. Evans, and D. F. S. Natusch, "Microscopic Investigations of Coal Fly Ash Particles."  
Presented by R. W. Linton at the 10th Annual Conference of the Microbeam Analysis Society, Las Vegas, Nevada.
- August 1975 R. W. Linton, A. Loh, D. F. S. Natusch, C. A. Evans, and P. Williams, "Surface Predominance of Trace Elements in Airborne Particles."  
Presented by R. W. Linton at the 10th Annual Conference of the Microbeam Analysis Society, Las Vegas, Nevada.
- September 1975 D. F. S. Natusch and T. M. Thorpe, "Gas Evolution Analysis: A Potentially Powerful Tool for Trace Metal Speciation."  
Presented by T. M. Thorpe at the Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) in Indianapolis, Indiana.
- September 1975 J. M. McNurney, R. W. Larimore, and M. J. Wetzel, "Distribution of Lead in the Sediments and Fauna of a Small Midwestern Stream."  
Presented by J. M. McNurney at the 15th Hartford Symposium in Richland, Washington.
- October 1975 G. Provenzano, "Cost-Risk-Benefit Analysis and the Removal of Lead Additives from Gasoline."  
Presented by author at the International Conference on Heavy Metals in the Environment, in Toronto, Ontario.
- October 1975 D. F. S. Natusch, C. A. Evans, P. K. Hopke, A. Loh, and R. Linton, "Characterization of Trace Elements in Coal Fly Ash."  
Presented by D. F. S. Natusch at the International Conference on Heavy Metals in the Environment, in Toronto, Ontario.
- October 1975 G. L. Wheeler, K. A. Reinbold, and G. L. Rolfe, "TELOC: A Model of the Effects of Lead on Corn."  
Presented by G. L. Wheeler at the International Conference on Heavy Metals in the Environment, in Toronto, Ontario.

## PUBLICATIONS

The following is a listing of publications and theses produced since the beginning of the project in 1970. The entries are arranged by year of publication.

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- Shukla, S. S., and H. V. Leland. 1973. Heavy metals: a review of lead. *Journal of the Water Pollution Control Federation* 45: 1319-31.
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- Rolfe, G. L., and J. C. Jennett. 1973. Environmental lead distribution in relation to automobile and mine and smelter sources. *Proceedings of the International Conference on Heavy Metals in the Aquatic Environment*. Nashville: Vanderbilt University.
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- Hassett, J. J., J. E. Miller, and D. E. Koeppe. Uptake of cadmium by corn.
- Hassett, J. J., J. E. Miller, and D. E. Koeppe. Interaction of lead and cadmium on corn root growth and uptake of lead and cadmium by roots.
- Miller, J. E., J. J. Hassett, and D. E. Koeppe. Interaction of lead and cadmium on metal uptake and growth by corn plants. (To be submitted to *Journal of Environmental Quality*.)
- Stevenson, F. J. Stability constants of  $Pb^{2+}$  and  $Cd^{2+}$  complexes with humic acids. (To be submitted to *Soil Science of America*.)
- Stevenson, F. J. The nature of divalent transition metal complexes of humic acids as revealed by potentiometric titration. (To be submitted to *Soil Science of America*.)
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DissertationsPh.D.

Will B. Betchart: "Optimum Sample Intervals for Water Quality Monitoring"

Kenneth W. Boyer: "Analysis of Auto Exhaust Particulates"

Race Li-Chan Kao: "Lead Toxicity in Experimental Animals"

George Provenzano: "The Economics of Environmental Quality Management: A General Systems Approach"

Gary L. Rolfe: "Lead Uptake of Selected Tree Seedlings"

Noel Watkins: "Cathodic Stripping Coulometry of Lead"

J. R. Wallace: "The Chemical and Physical Characterization of Airborne Particulate Matter"

Andrew Loh: "Electron Microscopic and Microprobe Analyses of Airborne Particles"

R. E. Polomsky: "Lead Levels in the Air, Soil, and Dust of an Isolated Urban Region"

Robert E. Lamb: "The Chemical Characterization of Airborne Particles"

Thomas M. Thorpe: "Determination of Trace Inorganic Species in Environmental Samples"

M.S.

John McNurney - "Benthic Invertebrates as Indicators of Lead Pollution in a Stream Ecosystem" - Special Problem Report - Environmental Engineering (student of R. W. Larimore)

L. L. Bonen - "The Interaction of Lead Chloride with the Erythrocyte Membrane and Membrane Lipids" (student of G. L. Jendrasiak)

J. A. Baker - "Aufwuchs Accrual and Lead Incorporation in a Small Polluted River" (student of H. V. Leland)

R. L. Dawson - "Trace Elements in Coal Fly Ash" (student of D. F. S. Natusch)

J. A. Miller - "Simultaneous Determination of Inorganic and Organic Mercury Bisequential Borohydride Reduction and Subsequent Analysis by the Cold Vapor Technique of Atomic Absorption Spectroscopy" (student of D. F. S. Natusch)



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